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(54) CHARGE INJECTION ASSISTANT AND ORGANIC ELECTROLUMINESCENCE DEVICE CONTAINING THE SAME

LADUNGSINJEKTIONSHILFE UND SIE ENHALTENDE ORGANISCHE ELEKTROLUMINESZENTE
VORRICHTUNG.

AIDE D'INJECTION DE CHARGE ET DISPOSITIF ELECTROLUMINESCENT ORGANIQUE LE
CONTENANT

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Description**TECHNICAL FIELD**

5 [0001] The present invention relates to a novel charge injection auxiliary material and an organic electroluminescence device containing the same. More particularly, it pertains to a charge injection auxiliary material capable of enhancing charge injecting properties which is a derivative of stilbene, distyrylarylene or tris(styrylarylene) and an organic electroluminescence device having a lowered applied voltage, an enhanced light emission efficiency and a prolonged service life which contains the above-mentioned charge injection auxiliary material.

BACKGROUND ART

15 [0002] In recent years, it has been desired that an organic electronic device such as electrophotographic photoreceptor, organic electroluminescence device (herein-after sometimes abbreviated to "organic EL device"), organic transistor, organic sensor and the like be capable of stably and efficiently injecting electric charge from an electrode or charge generating layer to a charge transporting layer. Examples of such device capable of stably and efficiently injecting electric charge include a device comprising a positive-hole injecting layer having carbon black dispersed therein which layer is interposed between a type-P photoconductor layer and a supporting substrate (refer to Japanese Patent Application Laid-Open No.12848/1984) and a device improved in charge injecting properties which comprises two divisional charge transporting layers, whose layer on the side of a charge generating layer is composed of a polymer layer having a distyryl compound dispersed therein (refer to Japanese Patent Application Laid-Open No.157660/1991). However, the above-mentioned devices have been complicated in production because of the necessity of adding a new layer to the device.

20 [0003] In addition, there is disclosed an organic EL device technology which enhances a positive-hole injecting efficiency into an organic light-emitting layer by the use of a injecting layer comprising an aromatic tertiary amine (refer to Japanese Patent Application Laid-Open No. 295695/1988). Nevertheless the above-disclosed device does not fully satisfy an electric power conversion efficiency and light-emitting efficiency. Thus, there is required an EL device capable of being driven by a lower voltage in order to enhance the power conversion efficiency and light-emitting efficiency of the device.

25 [0004] There is also disclosed an organic EL device technology which constitutes a light-emitting layer by mixing a styrylamine derivative being a positive-hole transporting material and also a light emitting material with an oxadiazole derivative being an electron transporting material (refer to Japanese Patent Application Laid-Open No.250292/1990). However, the aforesaid technology relates to the incorporation of an oxadiazole derivative into a light emitting layer comprising a styrylamine to impart electron injecting properties to the layer, and discloses nothing about such function 30 of a charge injection auxiliary material that improves charge injecting properties by adding a slight amount of a styrylamine to a light emitting layer to an electron transporting layer.

35 [0005] There are known an EL device having an organic light-emitting layer in which 8-hydroxyquinoline aluminum complex as the host is doped with a slight amount of a fluorescent substance (refer to Japanese Patent Application Laid-Open No.264692/1988) and an organic light-emitting layer in which 8-hydroxyquinoline aluminum complex as the host is doped with a quinacridone-based pigment (refer to Japanese Patent Application Laid-Open No.255190/1991). Nevertheless, the above-mentioned dopant do not function as a charge injection auxiliary material.

DISCLOSURE OF THE INVENTION

40 [0006] Under such circumstances, intensive research and investigation were made by the present inventors in order to develop a charge injection auxiliary material capable of enhancing charge injecting properties by adding a slight amount thereof in a functional layer such as a light-emitting layer in an organic electron device. As a result, it has been found by the present inventors that a derivative of stilbene, distyrylarylene or tris(styrylarylene) each having electron 45 donating property is useful as a charge injection auxiliary material and that an organic electroluminescence device containing the aforesaid charge injection auxiliary material and having an energy gap in a light-emitting layer higher than that in said charge injection auxiliary material is lower in applied voltage, enhanced in luminous efficiency and prolonged in service life. The present invention has been accomplished on the basis of the aforesated finding and information.

50 [0007] Specifically the present invention provides a charge injection auxiliary material for use in an organic electron device wherein a functional layer composed of a positive-hole transporting organic host substance is subjected to positive-hole injection from an external layer by incorporating said material in said functional layer which material is a derivative of stilbene, distyrylarylene or tris(styrylarylene).

55 [0008] In addition, the present invention provides an organic electroluminescence device which comprises the above-

mentioned charge injection auxiliary material and the light emitting layer characterized in that the ionization energy of the charge injection auxiliary material is smaller than the ionization energy of the light emitting layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Fig. 1 is a schematic illustration showing the energy level in an organic electron device. Fig. 2 is a schematic illustration showing the energy level in an organic electroluminescence device. In Fig. 1, symbol 11 is conduction level of functional layer, symbol 12 is valence level of functional layer, symbol 13 is valence level of charge injection auxiliary material, and symbol 14 is work function of anode or valence level of external layer. In Fig. 2, symbol 21 is conduction level of light emitting layer, symbol 22 is valence level of light emitting layer, symbol 23 is valence level of charge injection auxiliary material, symbol 24 is work function of anode, and symbol 25 is work function of cathode.

THE MOST PREFERRED EMBODIMENT TO CARRY OUT THE INVENTION

[0010] The charge injection auxiliary material according to the present invention is employed for the purpose of enhancing the charge injecting properties at the same electric field strength and injecting still more amount of charge in the case where positive holes are injected from an external layer into a positive hole transporting organic host substance. The amount of the charge injection auxiliary material to be added in the organic host layer is 1% or less by weight, preferably 0.05 to 9% by weight based on the weight of the positive-hole transporting organic host substance.

[0011] Accordingly, a charge injection auxiliary material is distinguished from a charge transporting material, namely a charge transporting material in a photosensitive body, a light emitting material in an organic EL device, a semiconductor in an organic transistor, and is a material used for the purpose of enhancing charge injecting properties by adding itself in the above-mentioned functional layer comprising the organic positive-hole transporting host substance as the principal component.

[0012] In addition, the term "functional layer" signifies a layer which preserves the function of transporting or injecting positive holes and is exemplified by a positive-hole injecting layer, positive-hole transporting layer, light emitting layer and electron barrier layer.

[0013] In the following, the function of the charge injection auxiliary material will be described with reference to Fig. 1.

[0014] Fig. 1 is a schematic illustration showing the energy level in an organic electron device. In the case where positive holes are injected from the energy level 14 to the energy level 12, the energy level barrier due to the difference between the energy levels 12 and 14 must be surmounted. When the charge injection auxiliary material having an energy level 13 is added in the functional layer, positive holes are more easily injected at the energy level 13, and the movement of positive holes to the level 12 takes precedence over the movement thereof within the level 13, since a slight amount of the charge injection auxiliary material is already dispersed in the functional layer. Thereby the charge injecting properties are enhanced. The charge injection auxiliary material according to the present invention is excellent in charge injection auxiliary function.

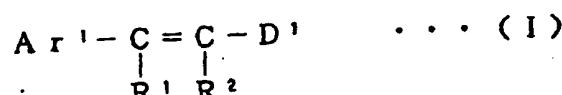
[0015] The styrene derivative to be used as the charge injection auxiliary material according to the present invention is a compound in which at least two aromatic rings are bonded by way of a vinyl group or a substituted vinyl group, and any of the aforementioned aromatic rings and vinyl group bears an electron donating group.

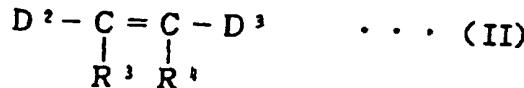
[0016] The distyrylarylene derivative is a compound in which two aromatic rings are bonded to one arylene group each by way of a vinyl group or a substituted vinyl group, and an electron donating group is contained.

[0017] In addition, the tris(styrylarylene) derivative is a compound in which three aromatic rings are bonded to one trivalent aromatic ring radical by way of a vinyl group or a substituted vinyl group, and an electron donating group is contained.

[0018] In the above-mentioned derivative containing an electron donating group in its molecular skeleton, the electron donating group is exemplified preferably by an alkoxy group having 1 to 10 carbon atoms, an aryloxy group having 6 to 10 carbon atoms and an amino group with a hydrocarbon radical having 1 to 30 carbon atoms.

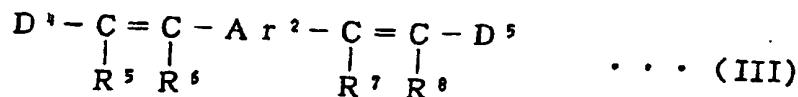
[0019] The particularly preferable derivatives in the present invention are the compounds represented by any of the following general formulae (I) to (VII), wherein (I) and (II) stand for a stilbene derivative, (III) and (IV) denote a distyrylarylene derivative, and (V) to (VII) indicate a tris(styrylarylene) derivative.





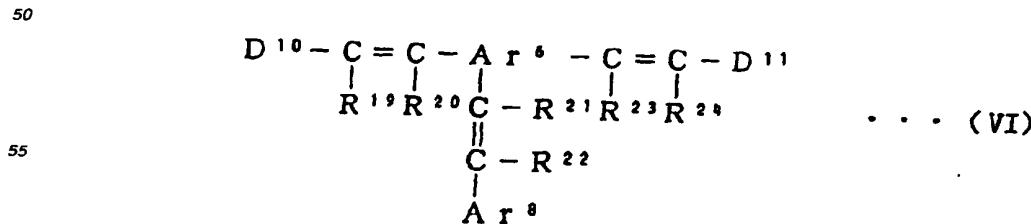
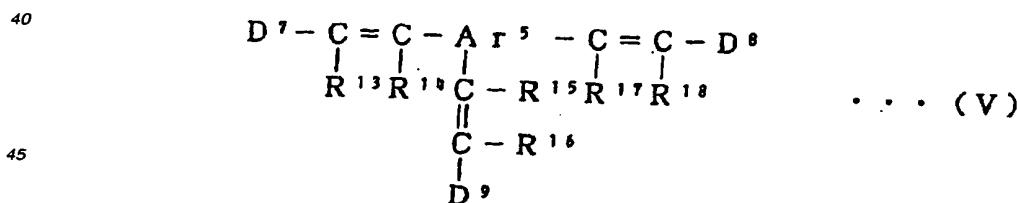
10 wherein Ar¹ is an aryl group having 6 to 20 carbon atoms, a thiienyl group or a bithienyl group, R¹ to R⁴ are each a hydrogen atom, an aryl group having 6 to 20 carbon atoms, a thiienyl group or a bithienyl group, R¹ and R², and R³ and R⁴ may each be same or different, respectively, D¹ to D³ are each an aryl group having 6 to 20 carbon atoms which is substituted with an electron donating group, a thiienyl group or a bithienyl group or a condensed polycyclic group having 10 to 30 carbon atoms, D² and D³ may be same or different, and Ar¹ and R¹ to R⁴ may each be unsubstituted or substituted with an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, an arylalkyl group having 7 to 10 carbon atoms or an amino group with

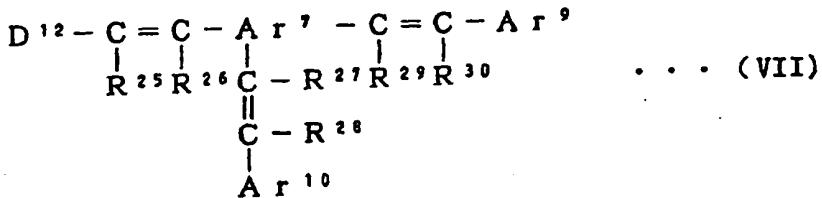
15 a hydrocarbon radical having 1 to 20 carbon atoms.



30 wherein Ar² and Ar³ are each an arylene group having 6 to 20 carbon atoms, a thiienylene group or a bithienylene group, Ar⁴ is an aryl group having 6 to 20 carbon atoms, a thiienyl group or a bithienyl group, R⁵ to R¹² are each a hydrogen atom, an aryl group having 6 to 20 carbon atoms, a thiienyl group or a bithienyl group, R⁵ to R⁸; and R⁹ to R¹² may each be same or different, respectively, D⁴ to D⁶ are each an aryl group having 6 to 20 carbon atoms which is substituted with an electron donating group, a thiienyl group or a bithienyl group or a condensed polycyclic group having 10 to 30 carbon atoms, D⁴ and D⁵ may be same or different, and Ar² to Ar⁴ and R⁵ to R¹² may each be unsubstituted or substituted with an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, an arylalkyl group having 7 to 10 carbon atoms or an amino group with

35 a hydrocarbon radical having 1 to 20 carbon atoms.





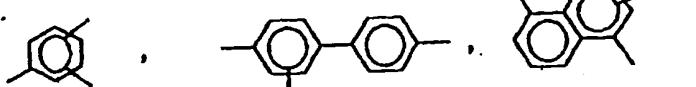
10 wherein Ar⁵ to Ar⁷ are each a trivalent aromatic ring radical having 6 to 24 carbon atoms, Ar⁸ to Ar¹⁰ are each an aryl group having 6 to 20 carbon atoms, a thiaryl group or a bithienyl group, Ar⁹ and Ar¹⁰ may be same or different, R¹³ to R³⁰ are each a hydrogen atom, an aryl group having 6 to 20 carbon atoms, a thiaryl group or a bithienyl group, R¹³ to R¹⁸; R¹⁹ to R²⁴; and R²⁵ to R³⁰ may be each same or different, respectively, D⁷ to D¹² are each an aryl group having to R¹⁸; R¹⁹ to R²⁴; and R²⁵ to R³⁰ may be each same or different, respectively, D⁷ to D¹² are each an aryl group having 15 6 to 20 carbon atoms which is substituted with an electron donating group, a thiaryl group or a bithienyl group or a condensed polycyclic group having 10 to 30 carbon atoms, D⁷ to D⁹, D¹⁰ and D¹¹ may be same or different, and Ar⁵ to condense R¹³ to R³⁰ may be each unsubstituted or substituted with an alkyl group having 1 to 10 carbon atoms, an Ar¹⁰ and R¹³ to R³⁰ may be each unsubstituted or substituted with an alkyl group having 1 to 10 carbon atoms, an arylalkyl group having alkoxyl group having 1 to 10 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, an arylalkyl group having 7 to 10 carbon atoms or an amino group with a hydrocarbon radical having 1 to 20 carbon atoms.

20 [0020] The aryl group having 6 to 20 carbon atoms in the above-mentioned general formulae (I) to (VII) is exemplified preferably by a phenyl group, biphenyl group, naphthyl group, pyrenyl group, terphenyl group, anthranyl group, tolyl group, xylyl group and monovalent group comprising stilbene.

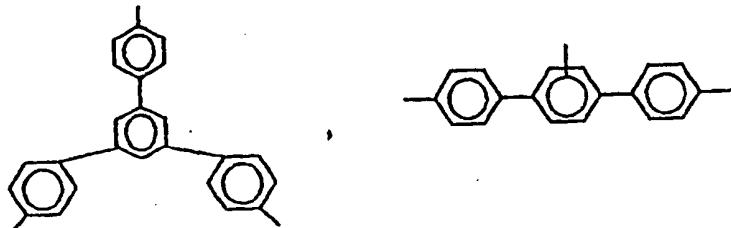
[0021] The arylene group having 6 to 20 carbon atoms therein is exemplified preferably by a phenylene group, bi-25 phenylene group, naphthylene group, anthranylene group, terphenylene group, pyrenylene group and divalent group comprising stilbene.

[0022] The trivalent aromatic ring radical having 6 to 24 carbon atoms is exemplified preferably by the following groups:

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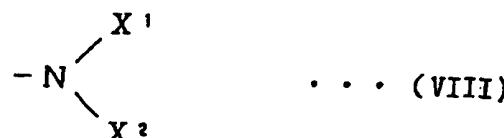
[0023] Examples of the aryloxy group having 6 to 20 carbon atoms as the above-mentioned substituent include a phenyloxy group, biphenyloxy group, naphthyoxy group, anthranyloxy group, terphenyloxy group and pyrenyloxy group; examples of the alkyl group having 1 to 10 carbon atoms include a methyl group, ethyl group, isopropyl group, tert-butyl group, pentyl group and hexyl group; examples of the alkoxy group having 1 to 10 carbon atoms include a methoxy group, ethoxy group, isopropoxy group, tert-butoxy group and pentyloxy group; and examples of the amino group with a hydrocarbon radical having 1 to 20 carbon atoms include a dimethylamino group, diethylamino group, diphenylamino group, phenylethylamino group, phenylmethylamino group, ditolylamino group, ethylphenylamino group, phenylnaphthyl amino group and phenylbiphenylamino group.

50 [0024] The D¹ to D¹² in the above-mentioned general formulae (I) to (VII) are each an aryl group having 6 to 20 carbon atoms which is substituted with an electron donating group, a thiaryl group or a bithienyl group or a condensed polycyclic group having 10 to 30 carbon atoms. The electron donating group as mentioned herein is exemplified pre-

erably by an alkoxy group having 1 to 10 carbon atoms, an aryloxy group having 6 to 20 carbon atoms, particularly preferably by an amino group with a hydrocarbon radical having 1 to 30 carbon atoms. The aforesaid amino group can be exemplified by the group represented by the general formula

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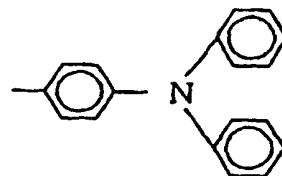
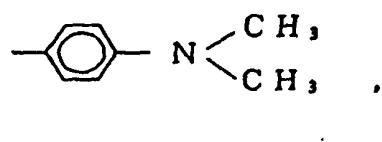


wherein X^1 to X^2 are each an alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 20 carbon atoms, a thienyl group, a bithienyl group or an arylalkyl group having 7 to 20 carbon atoms and may be same or different and be bonded to each other to form a saturated or unsaturated cyclic structure, and they may be a substituted alkyl group having 1 to 10 carbon atoms, a substituted alkoxy group having 1 to 10 carbon atoms, a substituted aryloxy group having 6 to 10 carbon atoms or a substituted arylalkyl group having 7 to 10 carbon atoms.

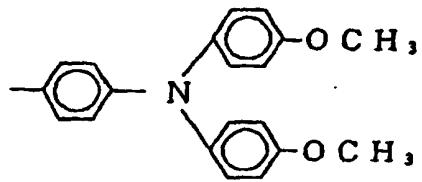
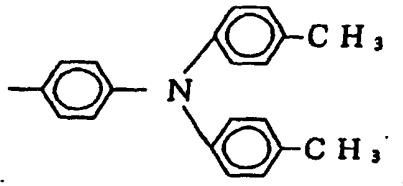
[0025] Preferable examples of the above-mentioned electron donating group include an alkoxy group or aryloxy group such as phenoxy group, biphenyloxy group, naphthoxy group, anthranyloxy group, terphenyloxy group, a hydrocarbon radical such as dimethylamino group, diethylamino group, diphenylamino group, phenylmethylamino group, phenylethylamino group, phenylmethylethylamino group, ditolylamino group, ethylphenylamino group, phenylphthylamino group and phenylbiphenylyl amino group. Specific examples of the D^1 to D^{12} include the following:

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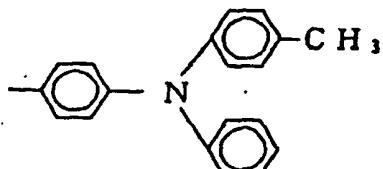
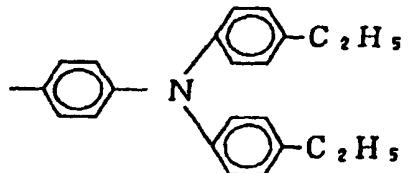


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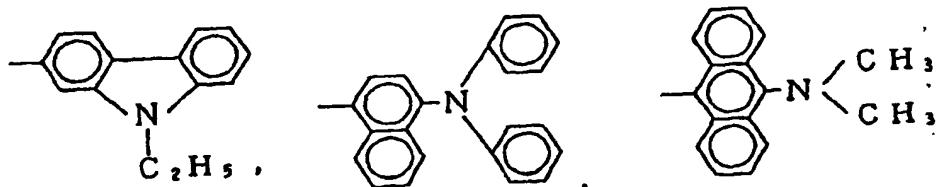


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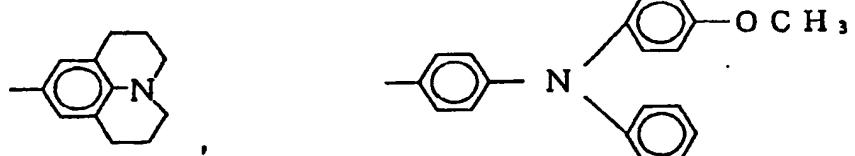


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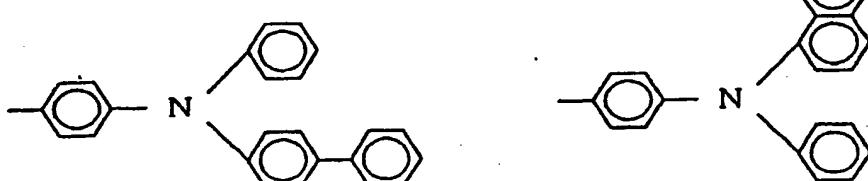
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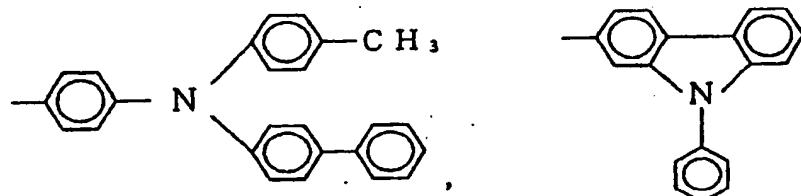
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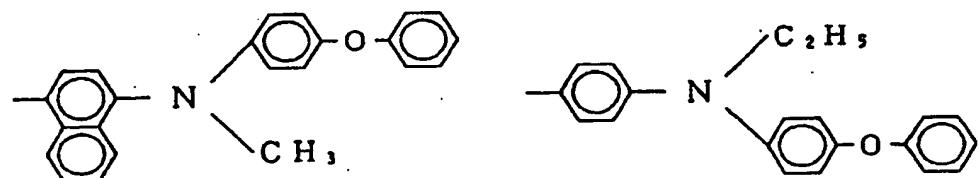
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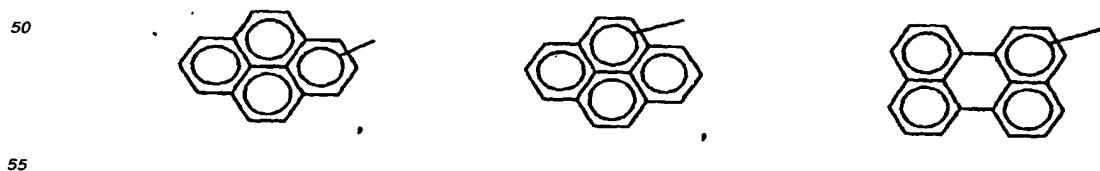
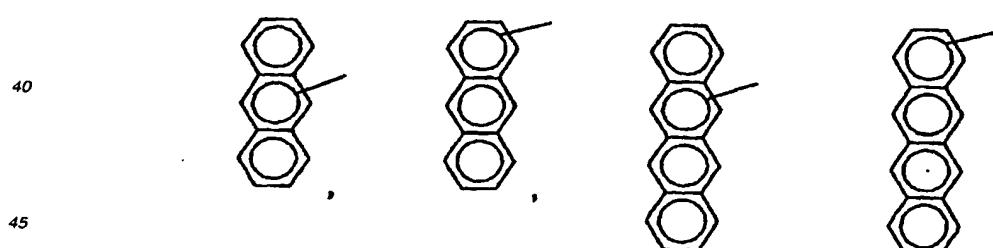
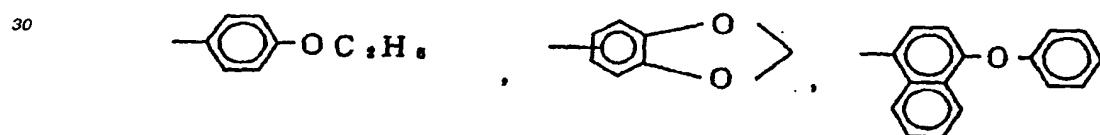
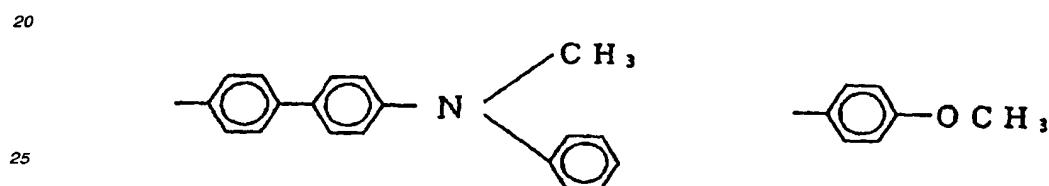
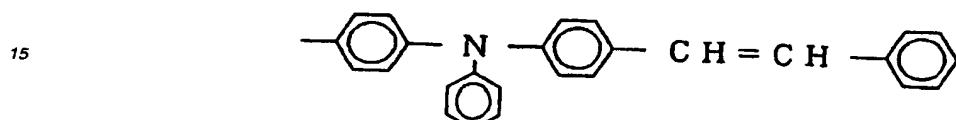
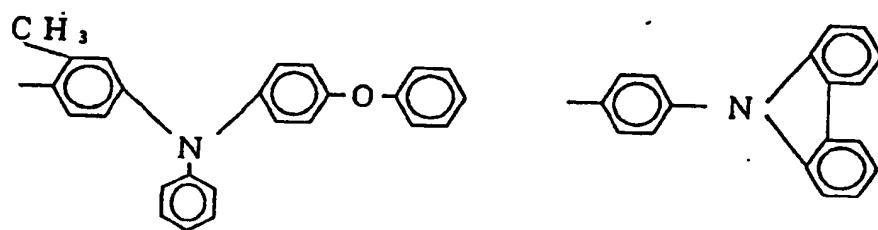
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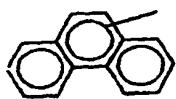


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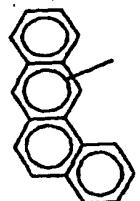




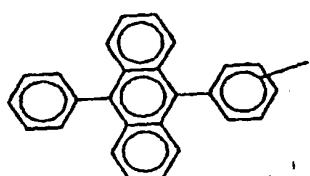
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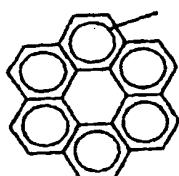
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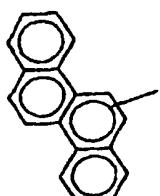
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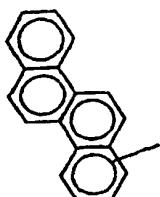
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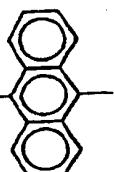
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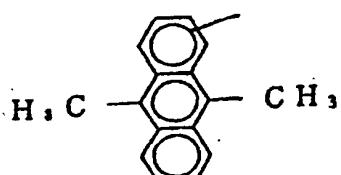
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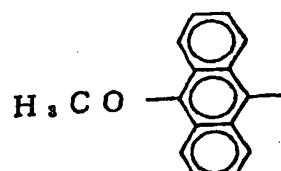
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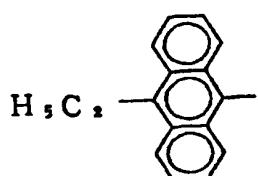
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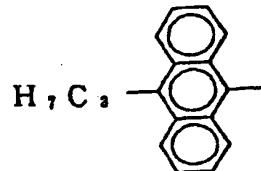
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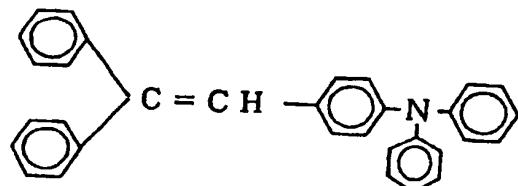
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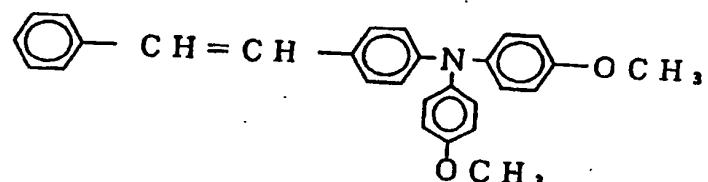


[0026] Specific examples of the compound represented by any of the general formulae (I) to (VII) include the following:



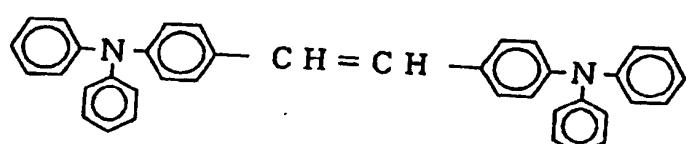
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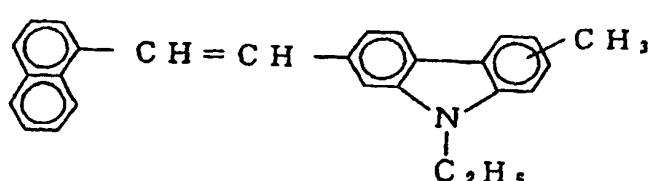
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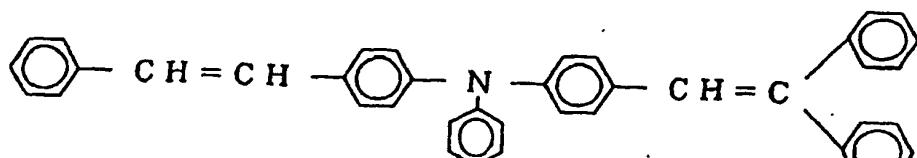
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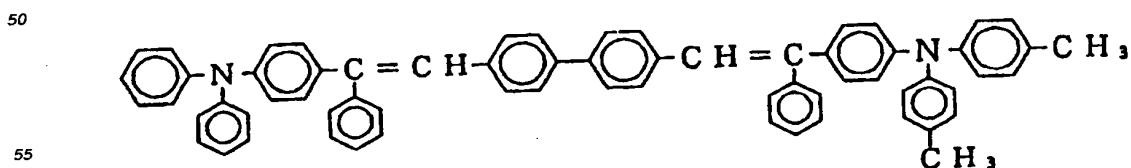
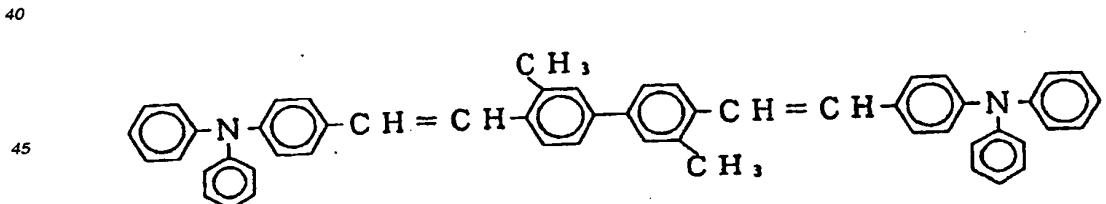
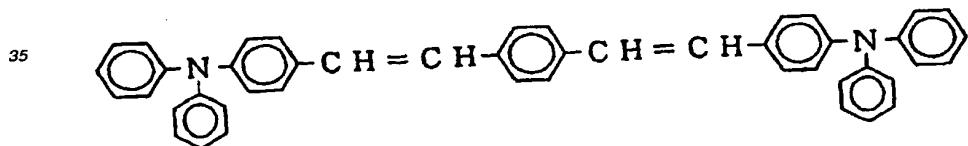
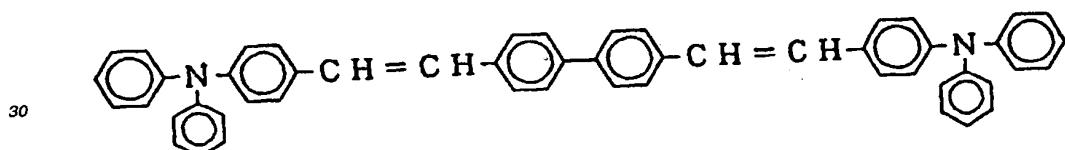
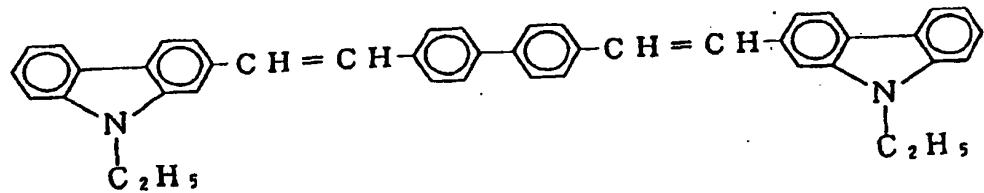
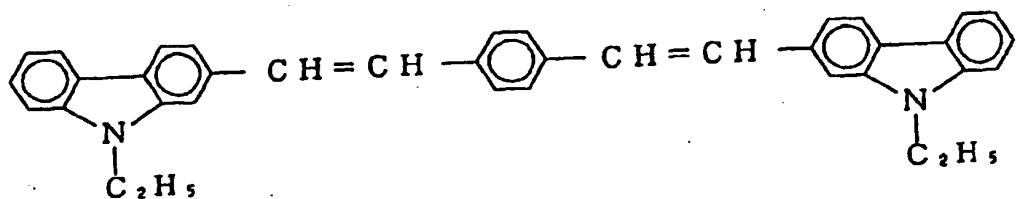
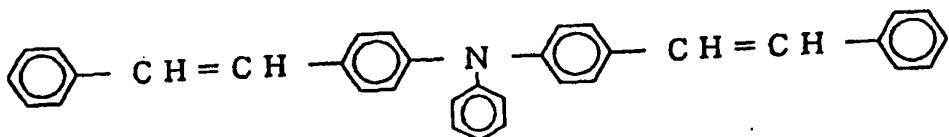
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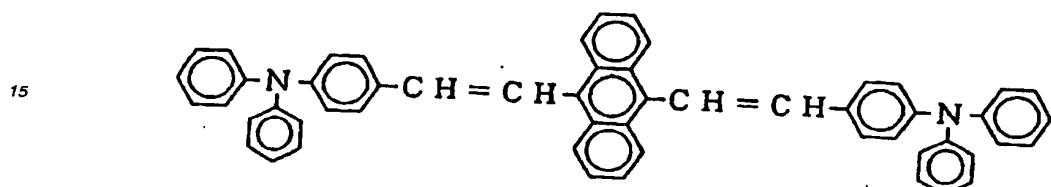
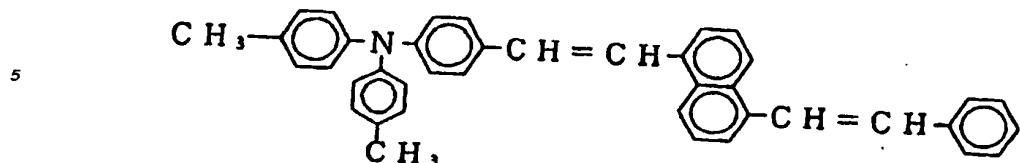


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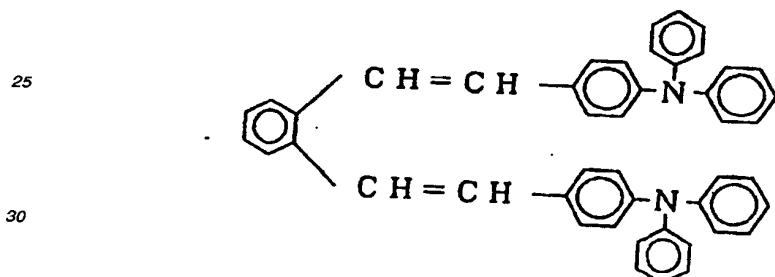
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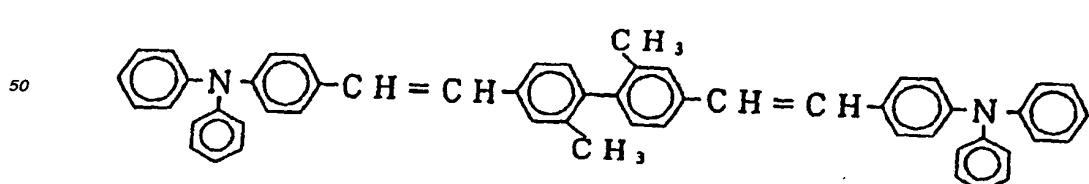
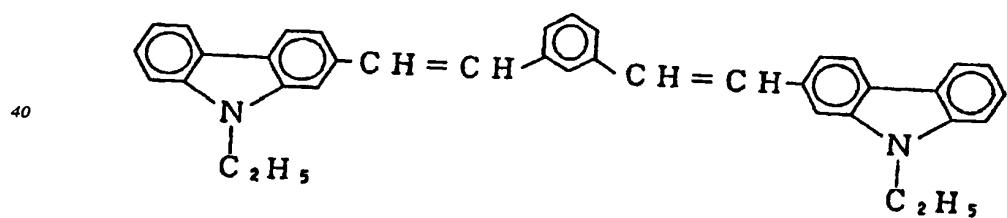


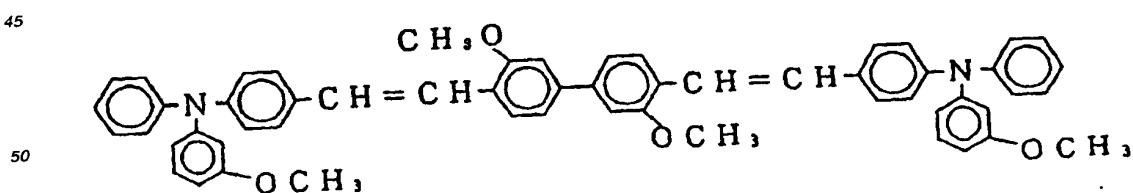
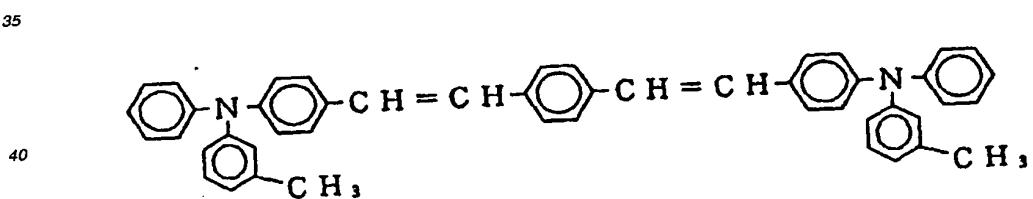
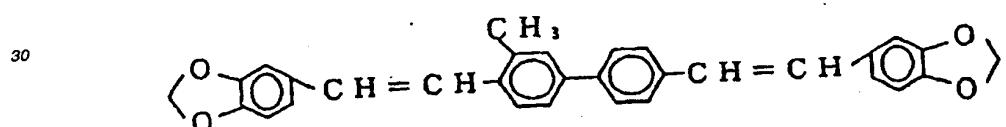
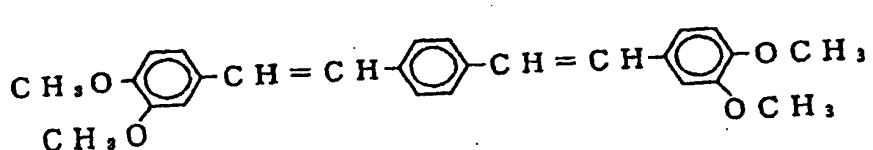
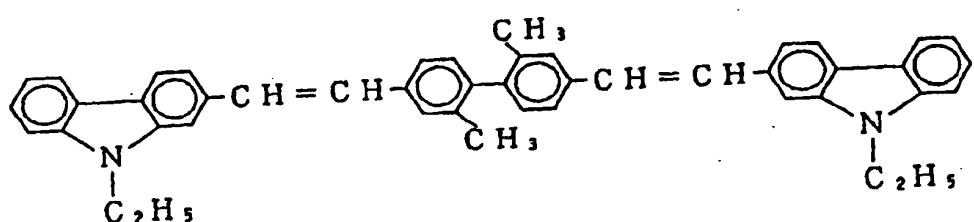
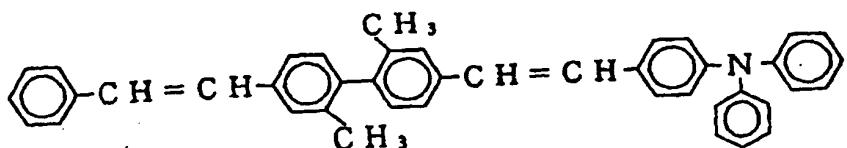


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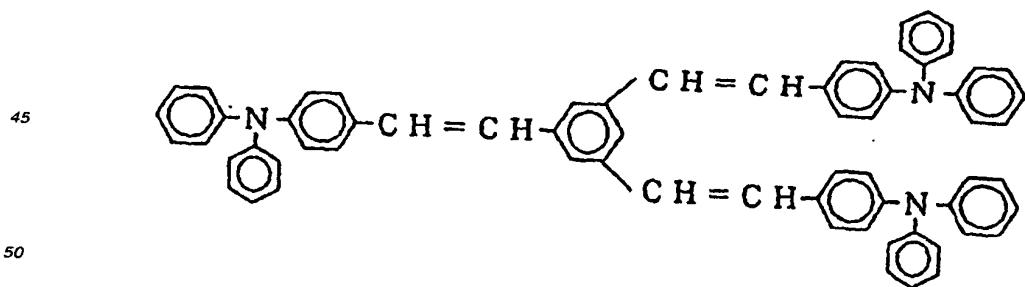
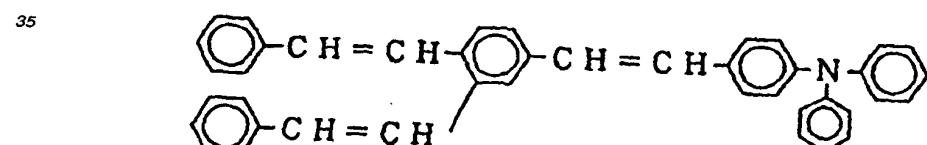
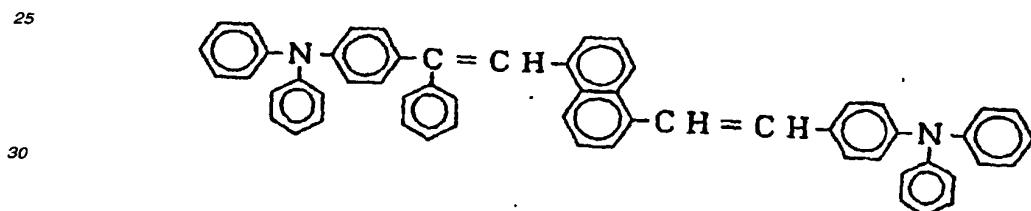
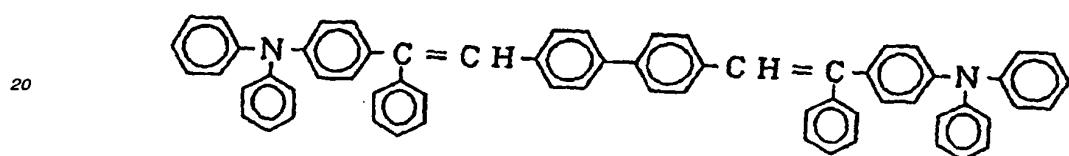
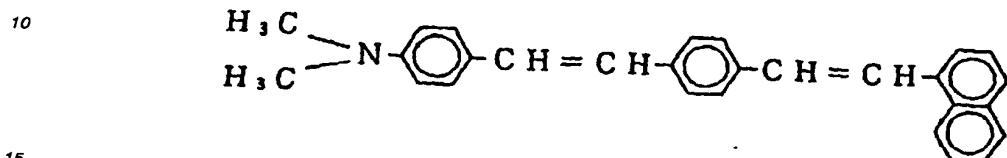
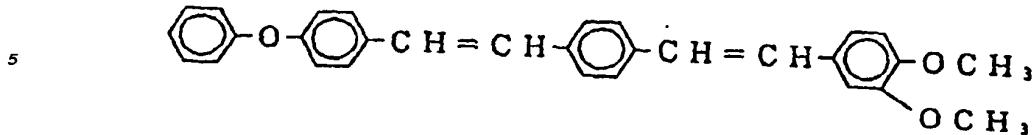


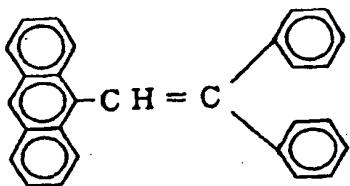
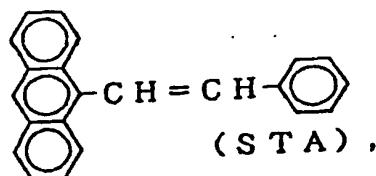
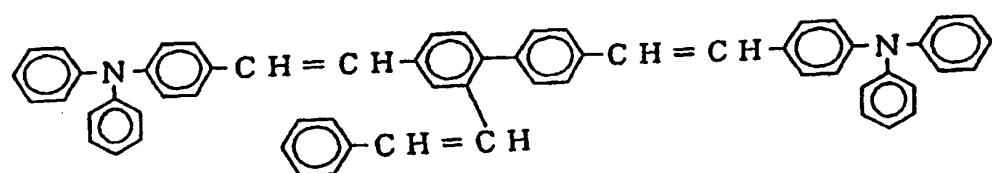
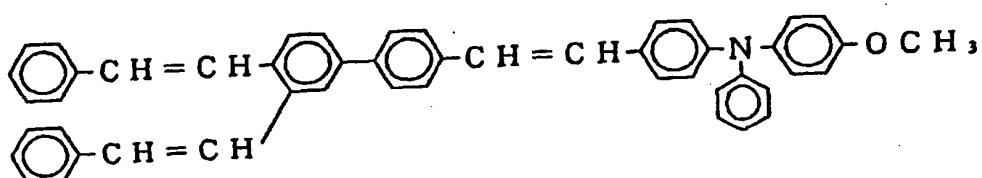
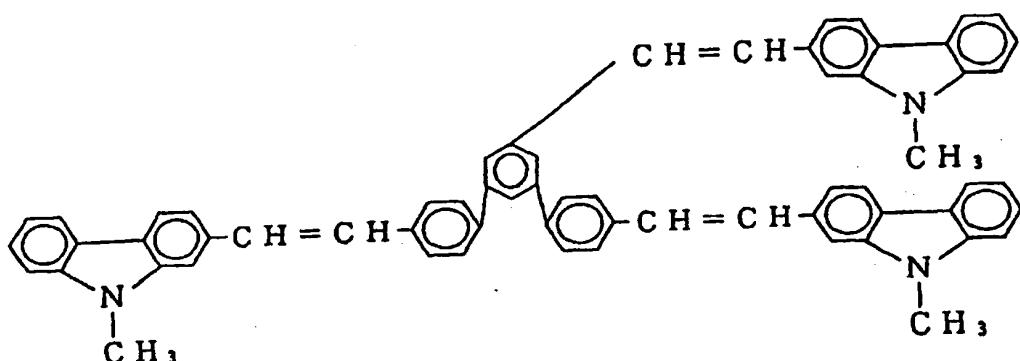
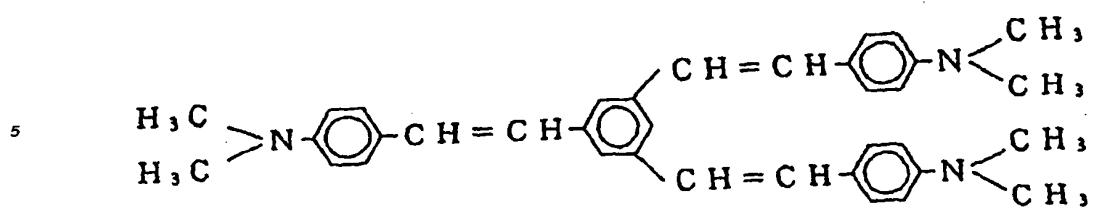
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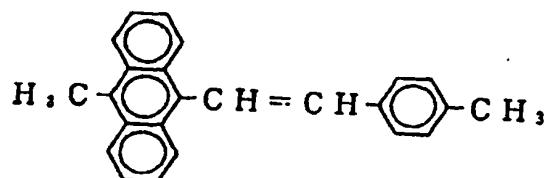


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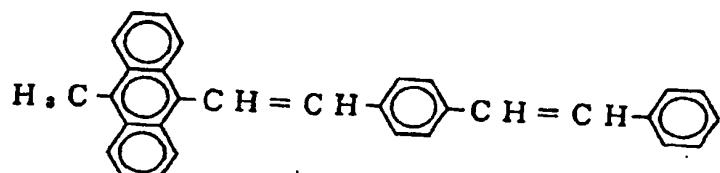


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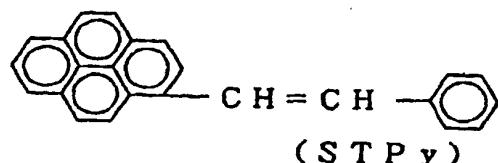
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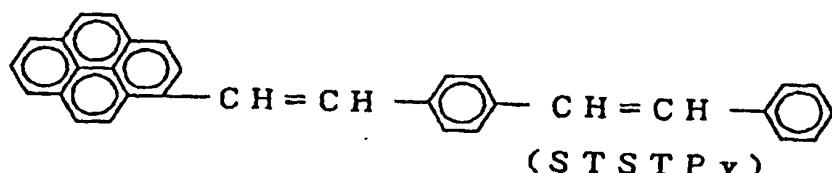
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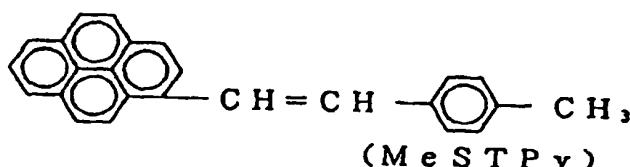
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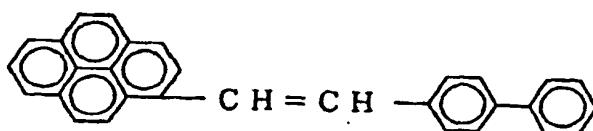


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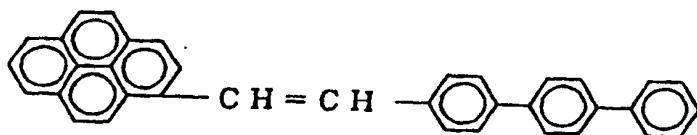
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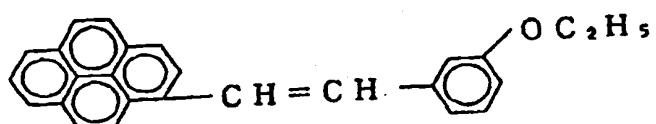
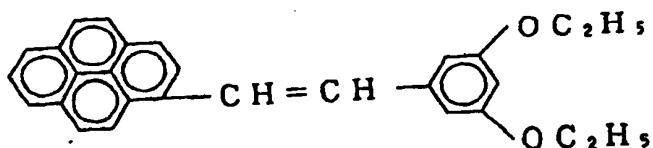


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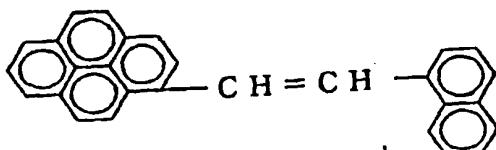


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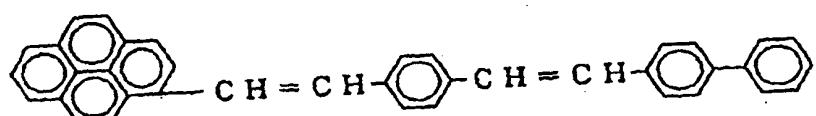




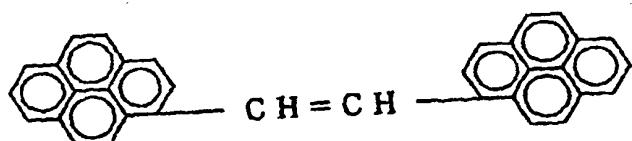
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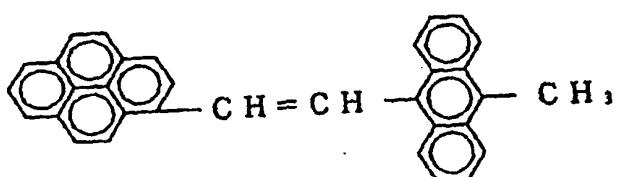
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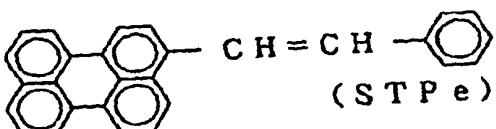
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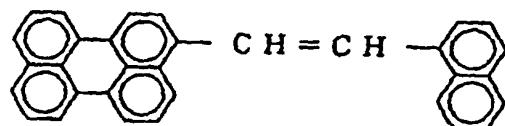
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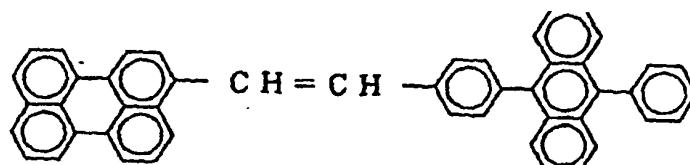


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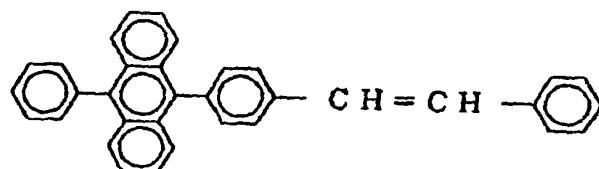
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[0027] Particularly preferable compound among the charge injection auxiliary materials represented by any of the general formulae (I) to (VII) is the distyrylarylene derivative represented by any of the general formulae (III) and (IV), which has a remarkable charge injection assistant function.

[0028] In the following, the principle of the charge injection auxiliary material when applied to an organic EL device will be described with reference to Fig. 2, which is an energy level drawing prepared for describing the principle of the charge injection auxiliary material in the organic EL device comprising an anode/a light emitting layer/a cathode.

[0029] Positive holes among the charges are injected under applied electric field at the valence electron level 23 of the charge injection auxiliary material, since it is easier than the injection at the valence level of the light emitting layer. Then, the positive holes try to move towards the cathode at the valence level of the light emitting layer, move at the valence level and recombine with the electrons moving at the conduction level injected from the cathode.

[0030] It is understood from the description that the charge injection auxiliary material according to the present invention makes it easy to inject the positive holes in the light emitting layer usually at an energy lower than the ionization energy of the light emitting layer.

[0031] Some of the charge injection auxiliary material has an energy gap smaller than that of the light emitting layer. In such a case, the excited state formed by the charge which has rejoined in the light emitting layer is transferred to the charge injection auxiliary layer.

[0032] Since the charge injection auxiliary material which has been dispersed in a slight amount according to the present invention has a high fluorescence yield, the quantum yield of the EL device using the charge injection auxiliary material according to the present invention is sometimes doubled or more.

[0033] As mentioned hereinbefore, the charge injection auxiliary material not only enables a decrease in applied voltage and improvement in quantum yield but also exhibits surprisingly remarkable effect on the stabilization of voltage as well as brightness of the EL device.

[0034] The point to which special attention should be paid is that the charge injection auxiliary material is added preferably in a slight amount in order to facilitate the movement at the valence level.

[0035] With regard to the organic EL device utilizing the above-mentioned charge injection auxiliary material, the following structures are possible in addition to the aforesaid structure.

(1) Anode/positive-hole injecting layer/light emitting layer/cathode

- (2) Anode/positive-hole injecting layer/light emitting layer/electron injecting layer/cathode
- (3) Anode/light emitting layer/electron injecting layer/cathode
- (4) Anode/organic semiconductor layer/light emitting layer/cathode
- (5) Anode/organic semiconductor layer/electron barrier layer/light emitting layer/cathode
- (6) Anode/positive-hole injecting layer/light emitting layer/adhesion improving layer/cathode

[0036] The objective device can be obtained by adding the charge injection auxiliary material according to the present invention to the above-mentioned light emitting layer, positive-hole injecting layer or organic semiconductor layer.

[0037] In the above-mentioned light emitting layer, positive-hole injecting layer, or organic layer, the invention in the above-mentioned light emitting layer, positive-hole injecting layer, or organic layer, the charge injection auxiliary material has a molecular structure similar to that in the light emitting layer (the host substance in the light emitting layer), as the case may be, but the similar molecular structure does not cause any problem. The host material occupies 81 % or more by weight of the light emitting material, and the charge injection auxiliary material occupies 19 % or less by weight of the light emitting material, preferably in the range of 0.5 to 5 % by weight based thereon. In addition, it is particularly preferable that the charge injection auxiliary material be lower than that of the light emitting material.

[0038] Moreover, it is particularly preferable that the difference in the ionization energy between the light emitting material, preferably the charge injection auxiliary material, and the light emitting material be lower than that of the light emitting material, preferably the charge injection auxiliary material be not less than 0.1 eV.

[0039] The charge injection auxiliary material according to the present invention functions as a fluorescent dopant in addition to the charge injection assistant effect. By the term fluorescent dopant is meant a substance which emits electrons in the region consisting of the host material.

in addition to the charge injection auxiliary material, light in response to the recombining of positive holes and electrons in the region consisting of the host material.

20 [0040] The present invention also provides an organic EL device which comprises the above-mentioned charge injection auxiliary material and the light emitting material having an energy gap more than the energy gap of said charge injection auxiliary material. It is preferable in said organic EL device that the energy gap of the charge injection auxiliary material be less than the energy gap of the light emitting layer by 0.1 eV or more. The suitable organic EL device is such that it emits light by being excited through the recombination of positive holes and electrons in the light emitting layer. Such organic EL device according to the present invention is characterized by lowered applied voltage, enhanced luminous efficiency and prolonged service life.

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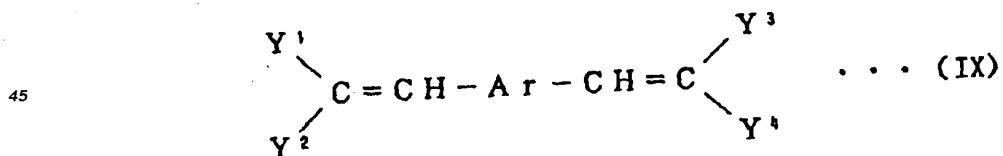
[0041] The charge injection auxiliary material according to the present invention is present in the functional layer of the organic electron device. In the case where the organic electron device is an organic EL device, said functional layer is the functional layer of the organic EL device. The organic EL device has the above-mentioned structures (1), (2) and (3).

30 the organic electron device. In the case where the organic electron device is a light emitting device, the organic electron device has a structure in which an electron injecting layer or a light emitting layer is provided on the organic semiconductor layer, and the organic electron device has a structure in which a positive-hole injecting layer or a light emitting layer is provided on the organic semiconductor layer. The organic electron device has a structure in which a barrier layer or a light emitting layer is provided on the organic semiconductor layer.

[0042] The light emitting layer in the aforestated organic EL device, as is the case with ordinary light emitting layer, has the function (it is capable of injecting positive hole from an anode or positive hole injecting layer to the light emitting layer when a voltage is being applied); a trans-

[0042] The light emitting device of the present invention has a structure which possesses an injecting function (it is capable of injecting positive hole from an anode and besides injecting electron from a cathode or electron injecting layer at the time of voltage being applied); a transporting function (it is capable of moving positive hole and electron by electric field force); and light emitting function (it is capable of providing the rejoining field of positive hole and electron, thereby emitting light). The thickness of the functional layer can be determined suitably according to the conditions without specific limitation, and is preferably 1 nm to 10 μ m, particularly preferably 5 nm to 5 μ m.

40 nm to 10 μ m, particularly preferably 5 nm to 5 μ m.
[0043] As the preferable light emitting material (host material), mention can be made of the compound represented by the general formula (IX)



50 wherein Y¹ to Y⁴ indicate each a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, an aralkyl group having 7 to 8 carbon atoms, a substituted or unsubstituted aryl group having 6 to 18 carbon atoms, a substituted or unsubstituted cyclohexyl group, a substituted or unsubstituted aryloxy group having 6 to 18 carbon atoms, or an alkoxy group having 1 to 6 carbon atoms; therein, the substituent is an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, an aralkyl group having 7 to 8 carbon atoms, having 1 to 6 carbon atoms, an aryl group having 6 to 18 carbon atoms, an acyl group having 1 to 6 carbon atoms, an acyloxy group having 1 to 6 carbon atoms, a carboxyl group, a styryl group, an arylcarbonyl group having 6 to 20 carbon atoms, an aryloxy- to 6 carbon atoms, a carbonyl group having 6 to 20 carbon atoms, an alkoxy carbonyl group having 1 to 6 carbon atoms, a vinyl group, an anilinocarbonyl group, a carbamoyl group, a phenyl group, a nitro group, a hydroxyl group or a halogen; these substit-

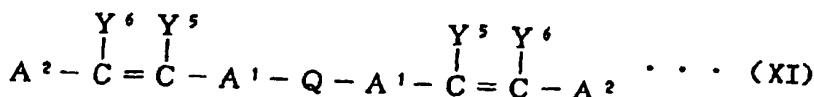
uents may be used solely or in plural; Y¹ to Y⁴ may be identical to or different from one another, and Y¹ and Y² and Y³ and Y⁴ may combine with groups substituting each other to form a substituted or unsubstituted saturated five-membered ring or a substituted or unsubstituted saturated six-membered ring; Ar indicates a substituted or unsubstituted arylene group having 6 to 20 carbon atoms, which may be mono-substituted or polysubstituted, and in which its bonding position may be any of ortho-, para- and meta-; however, when Ar is an unsubstituted phenylene, Y¹ to Y⁴ is each selected from the group consisting of an alkoxy group having 1 to 6 carbon atoms, an aralkyl group having 7 to 8 carbon atoms, a substituted or unsubstituted naphthyl group, a biphenyl group, a cyclohexyl group, and an aryloxy group, general formula (X):

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wherein A and B indicate each a monovalent group which is obtained by removing a hydrogen atom from the compound represented by the above general formula (IX), and may be identical to or different from each other; Q indicates a divalent group breaking the conjugation, or general formula (XI)

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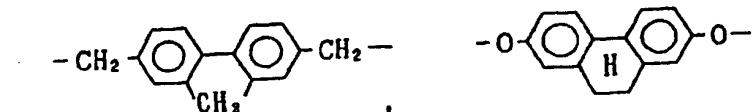
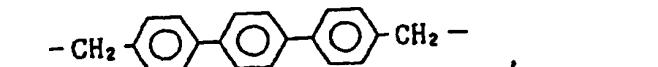
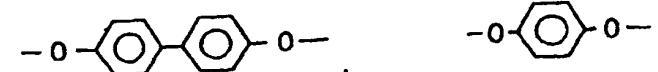
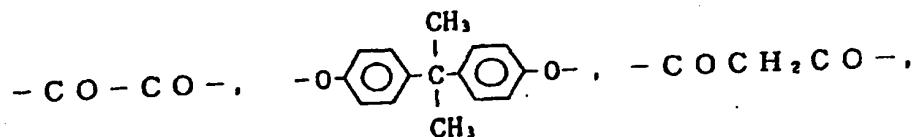
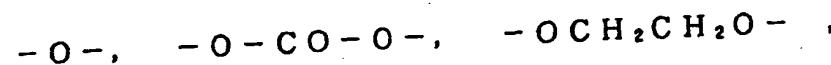
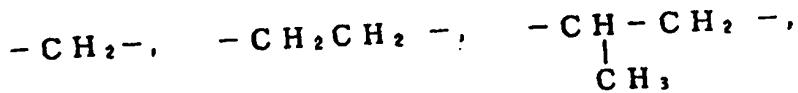
wherein A¹ indicates a substituted or unsubstituted arylene group having 6 to 20 carbon atoms or a divalent aromatic heterocyclic group; its bonding position may be any of ortho-, meta- and para-; A² is a substituted or unsubstituted aryl atom, a substituted or unsubstituted aryl group having 6 to 20 carbon atoms, a cyclohexyl group, a monovalent aromatic heterocyclic group, an alkyl group having 1 to 10 carbon atoms, an aralkyl group having 7 to 20 carbon atoms or an alkoxy group having 1 to 10 carbon atoms; Y⁵ and Y⁶ indicate each a hydrogen atom, a substituted or unsubstituted aryl group having 6 to 20 carbon atoms, a cyclohexyl group, a monovalent aromatic heterocyclic group, an alkyl group, an aryloxy group, an amino group or a phenyl group with or without a substituent; each substituent of Y⁵ may combine with A¹ to form a saturated or unsaturated five-membered ring or six-membered ring, and similarly each substituent of Y⁶ may combine with A² to form a saturated or unsaturated five-membered ring or six-membered ring; Q indicates a divalent group breaking a conjugation, [0044] The symbol Q in the general formulae (X) and (XI) indicates a divalent group breaking a conjugation. The conjugation therein is attributable to the delocalization of π -electron, and includes a conjugated double bond or a conjugation due to an unpaired electron or a lone electron-pair. Specific examples of Q include

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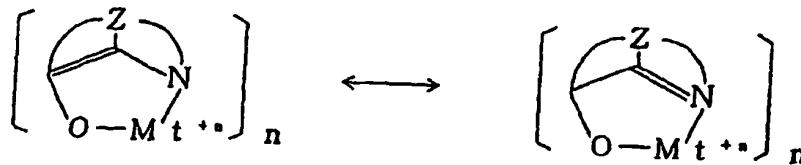


40 [0045] The divalent group breaking the conjugation is thus used in order that EL emission light obtained when the compound forming A or B shown in above (that is, the compound of general formula (IX)) is used solely as the organic EL device of the present invention and the EL emission light obtained when the compound represented by general formula (X) is used as the organic EL device of the present invention may be identical in color. In other words, said divalent group is used so that the wavelength of the light emitting layer using the compound represented by general formula (IX) or general formula (X) may not be shortened or lengthened. By combining with a divalent group to break conjugation, it is confirmed that the glass transition temperature (Tg) rises, and uniform pinhole free minute crystal or amorphous thin film can be obtained, improving the uniformity of light emission. Further, combining with a divalent group breaking the conjugation brings about advantages that EL emission is not long-waved, and synthesis or purification can easily be effected.

45 [0046] As another preferable light emitting material (host material), mention can be made of a metal complexe of 8-hydroxyquinoline or derivative thereof. Specific examples of them include metal chelated oxinoide compound containing a chelate of oxine (generally, 8-quinolinol or 8-hydroxyquinoline).

50 [0047] Such compound exhibits high level performance, and is easy to be formed into thin film. Examples of the oxinoide compounds satisfy the following structural formula.

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wherein Mt indicates a metal, n is an integer of 1 to 3, and Z indicates an atom required to complete at least two condensed aromatic ring, being located independently.

[0048] Therein the metal represented by Mt is a monovalent, divalent or trivalent metal, that is, an alkali metal such as lithium, sodium or potassium, an alkaline earth metal such as magnesium or calcium, or an earth metal such as boron or aluminum.

[0049] Generally any of monovalent, divalent and trivalent metals which are known to be useful chelated compounds can be used therein.

[0050] Z indicates an atom to form a hetero ring comprising azole or azine as one of at least two condensed aromatic rings. Herein, if necessary, another ring can be added to the above-mentioned condensed aromatic ring. Moreover, in order to avoid adding bulky molecules without improvement in function, the number of the atoms shown by Z is preferably kept to not more than 18.

[0051] Further, specific examples of the chelated oxinoide compounds include tris(8-quinolinol)aluminum, bis(8-quinolinol) magnesium, bis(benzo-8-quinolinol)zinc, bis(2-methyl-8-quinolato)aluminum oxide, tris(8-quinolinol)indium, tris(5-methyl-8-quinolinol)aluminum, 8-quinolinol lithium, tris(5-chloro-8-quinolinol)gallium, bis(5-chloro-8-quinolinol) calcium, tris(5,7-dichloro-8-quinolinol)aluminum and tris(5,7-dibromo-8-hydroxyquinolinol)aluminum.

[0052] The above-mentioned light emitting layer can be prepared by forming the above compound into thin film by a known method such as the vapor deposition method, the spin-coating method, the casting method or the LB method, and particularly, a molecular accumulated film is preferable. A molecular accumulated film therein is a thin film formed by depositing said compound from a gaseous state, or a thin film formed by solidification of said compound from a molten state. Usually, said molecular accumulated film is distinguished from a thin film (molecular built-up film) formed by the LB method by the difference in the aggregation structure or the higher-order structure, or the functional difference resulting therefrom.

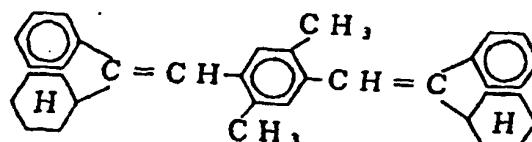
[0053] The above-mentioned light emitting layer can be formed by dissolving a binding agent such as a resin and said compound in a solvent to prepare solution, which is formed into thin film by the spin-coating method or the like.

[0054] The film thickness of the light emitting layer thus formed is not particularly limited, but can be determined appropriately according to the circumstances. Usually, it is preferably in the range of 1 nm to 10 μ m, particularly preferably 5 nm to 5 μ m.

[0055] Herein examples of compounds represented by any of the aforesaid general formulae (IX) to (XI) to be used as the above-mentioned light emitting layer are shown as follows.

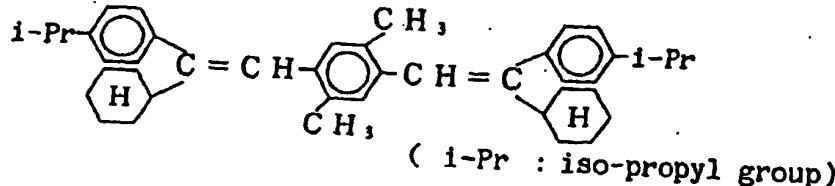
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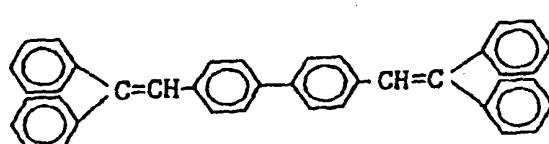
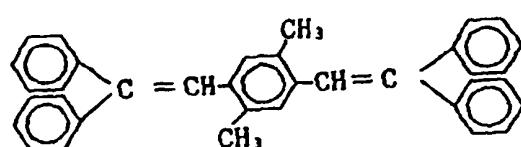
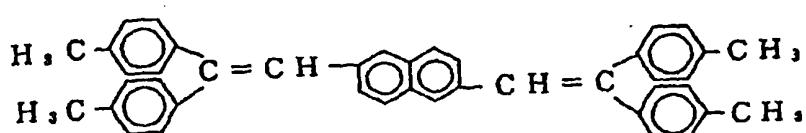
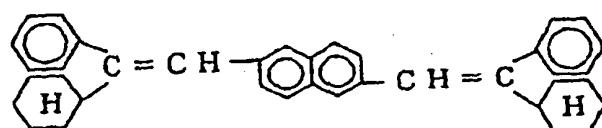
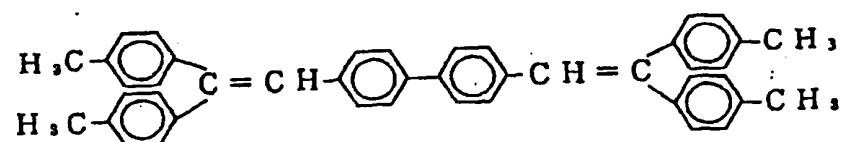
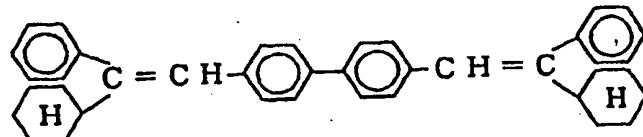
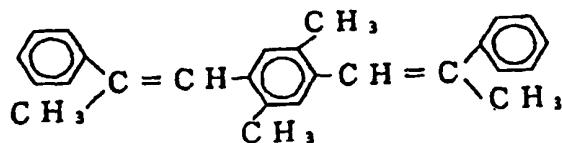
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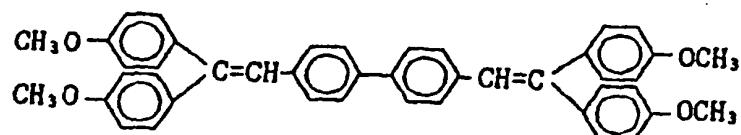
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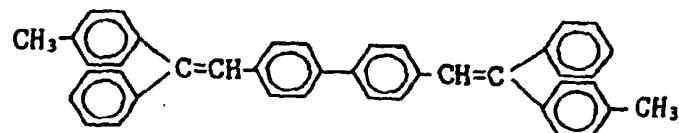


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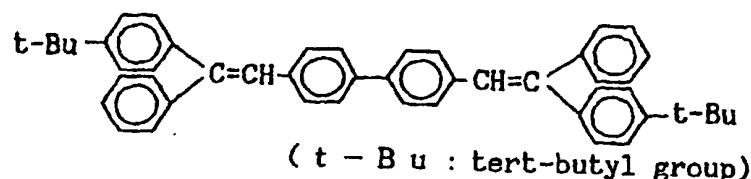


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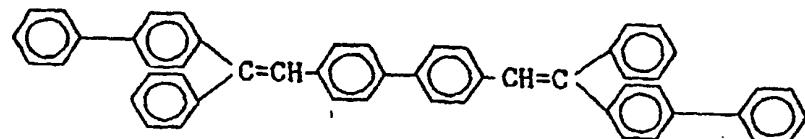
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(t - Bu : tert-butyl group)

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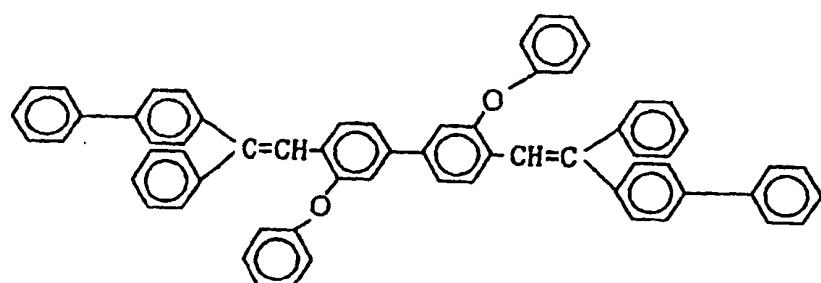
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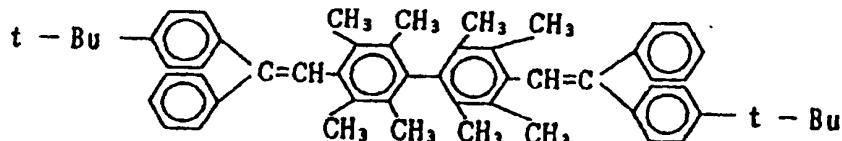
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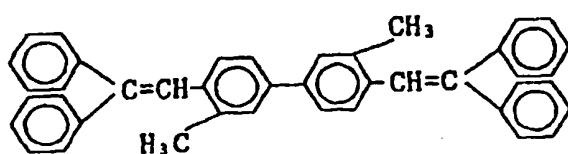
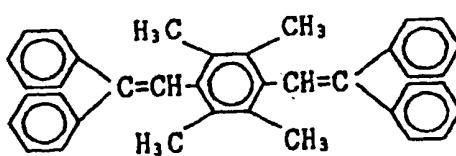
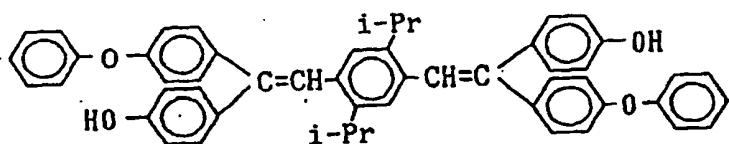
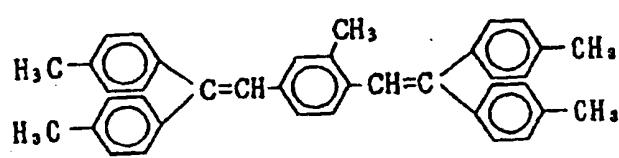
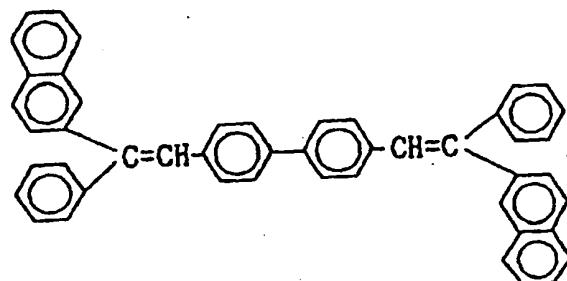
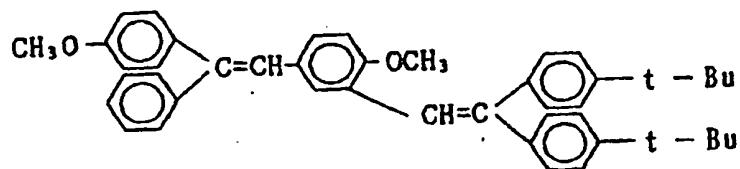
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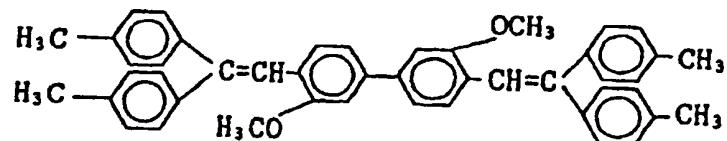
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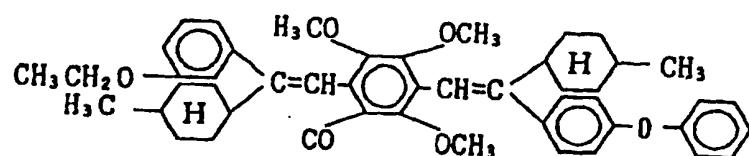


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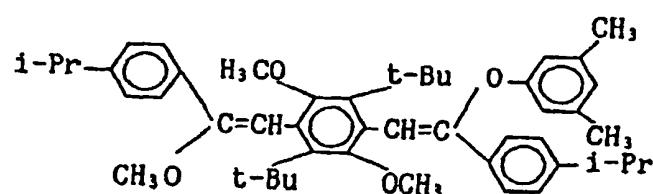
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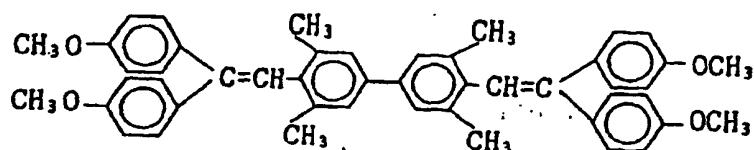
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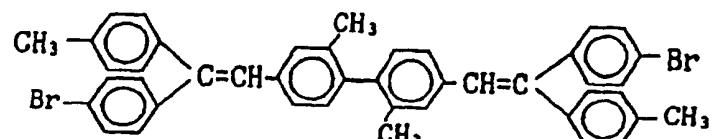
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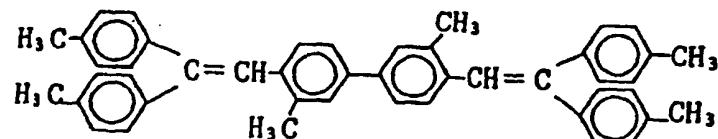


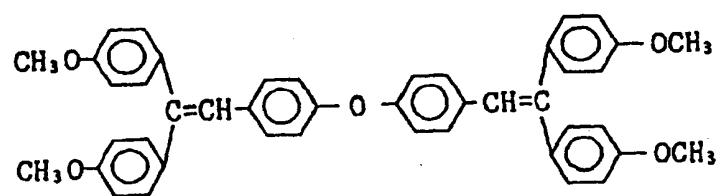
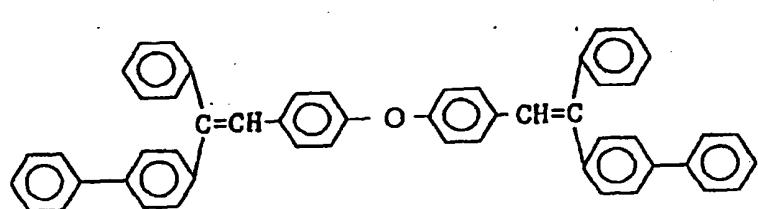
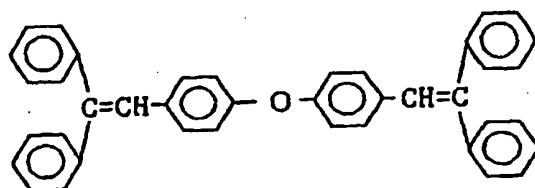
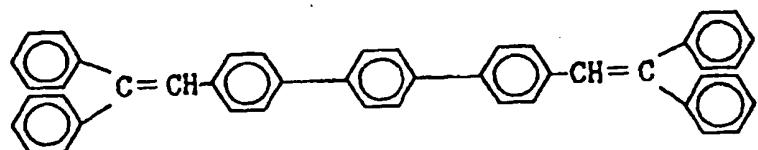
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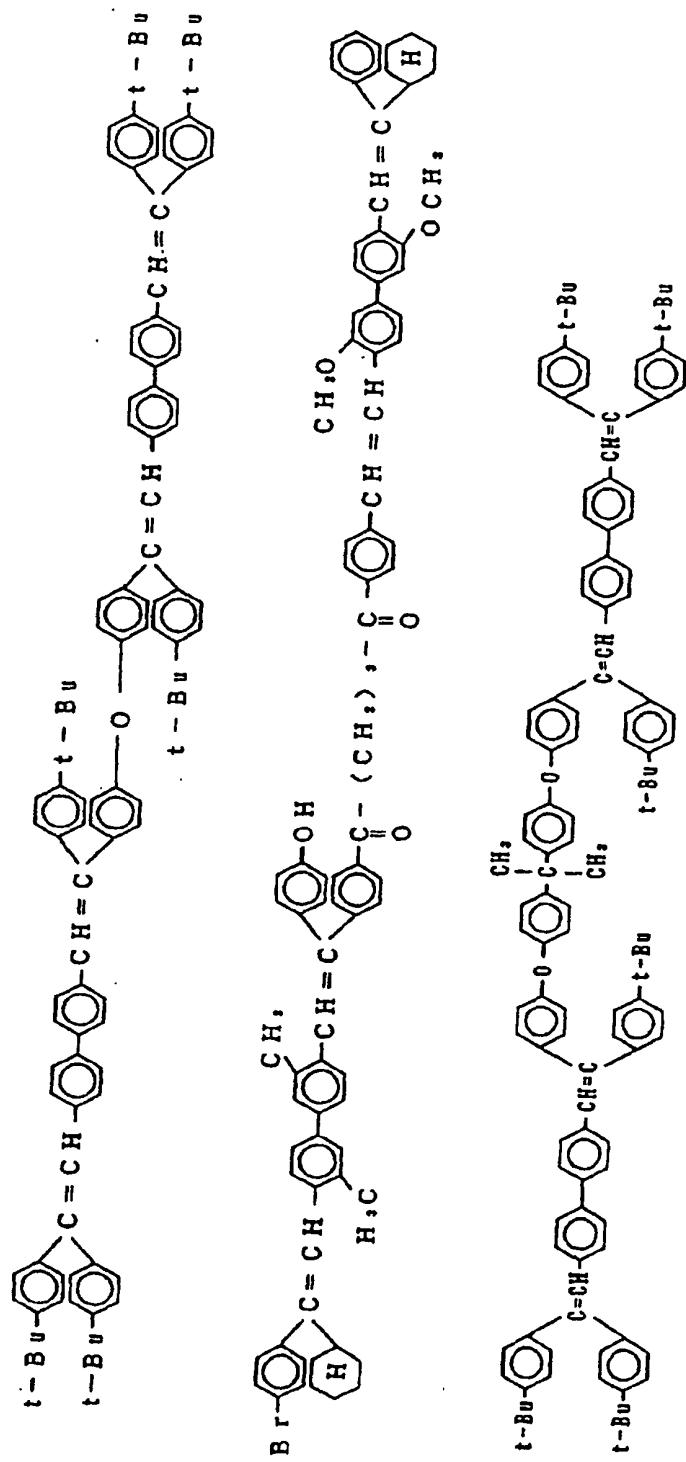
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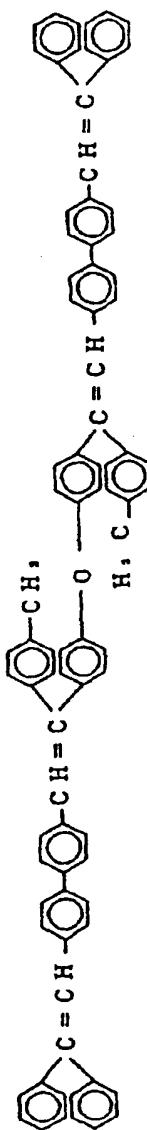
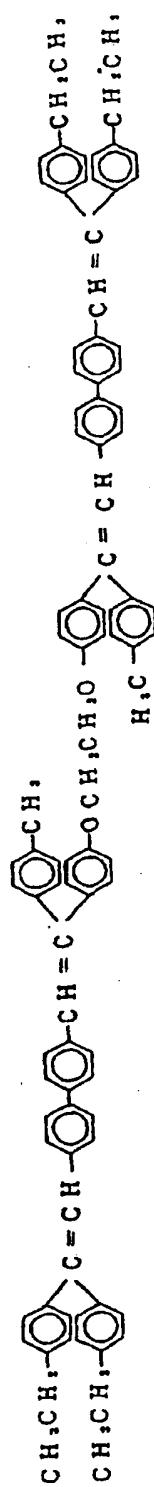
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[0056] As to the anode in the organic EL device of the present invention, a metal, an alloy, an electroconducting compound or a mixture thereof, all having a large work function (not less than 4 eV), is preferably used as an electrode material. Specific examples of these electrode materials are metals such as Au, and a dielectric transparent materials such as CuI, ITO, SnO_2 , and ZnO . The anode can be prepared by forming the electrode material into thin film by vapor deposition or sputtering. To obtain light emission from the electrode, it is preferable that the transmittance of the electrode be more than 10% and the resistance of the sheet as an electrode be not more than several hundred Ω/\square . The film thickness of the anode is usually in the range of 10 nm to 1 μm , preferably 10 to 20 nm, depending upon the material.

[0057] On the other hand, as the cathode, a metal, an alloy, an electroconducting compound or a mixture thereof, all having a small work function (not more than 4 eV) is preferably used as an electrode material. Specific examples of such electrode materials are sodium, a sodium-potassium alloy, magnesium, lithium, a magnesium-silver alloy, Al/ AlO_2 , indium, and rare earth metals. The cathode can be prepared by forming the electrode material into thin film by vapor deposition or sputtering. The resistance of the sheet as an electrode is preferably not more than several hundred Ω/\square . The film thickness is usually in the range of 10 nm to 1 μm , preferably 50 to 200 nm. In the EL device of the present invention, it is preferable that either anode or cathode be transparent or translucent because light emission is transmitted and obtained with a high efficiency by such property.

[0058] Next, the hole injecting layer in the present invention is not necessarily required for the present device, but is preferably used for the purpose of improving the emission performance. The preferable material of said hole-injecting layer is one which transports holes to the light emitting layer at a lower electric field, and still more preferably the mobility of holes is made at least $10^{-6}\text{cm}^2/\text{volt.sec}$ in at an applied electric field of 10^4 to 10^6 volt/cm. In order to stay electrons in the light emitting layer, an electron barrier layer may be used between the light emitting layer and the anode.

[0059] As the positive hole injecting material, arbitrary material can be selected and used from the conventionally used ones as the electric charges transporting material for holes and the known ones to be used for the hole-injecting layer of EL devices in conventional photo-conducting materials without specific limitation, provided that the material has the aforesaid favorable properties.

[0060] Examples of the materials for hole-injecting layer include triazole derivatives (described in the specification of US Patent No. 3,112,197, etc.), oxadiazole derivatives (described in the specification of US Patent No. 3,189,447, etc.), imidazole derivatives (described in Japanese Patent Publication No. 16096/1962, etc.), polyarylalkane derivatives (described in the specifications of US Patent Nos. 3,615,402, 3,820,989 and 3,542,544, and in Japanese Patent Publication Nos. 555/1970 and 10983/1976, and further in Japanese Patent Application Laid-Open Nos. 93224/1976, 17105/1980, 4148/1981, 108667/1980, 156953/1980 and 36656/1981, etc.), pyrazoline derivatives or pyrazolone derivatives (described in the specifications of US Patent Nos. 3,180,729 and 4,278,746, and in Japanese Patent Application Laid-Open Nos. 88064/1980, 88065/1980, 105537/1974, 51086/1980, 80051/1981, 88141/1981, 45545/1982, 112637/1979 and 74546/1970, etc.), phenylenediamine derivatives (described in the specification of US Patent No. 3,615,404, and in Japanese Patent Publication Nos. 10105/1976, 3712/1971 and 25336/1972, and further in Japanese

Patent Application Laid-Open Nos. 53435/1979, 110536/1979 and 119925/1979, etc.), arylamine derivatives (described in the specification of US Patent Nos. 3,567,450, 3,180,703, 3,240,597, 3,658,520, 4,232,103, 4,175,961 and 4,012,376, and in Japanese Patent Publication Nos. 35702/1974 and 27577/1964, and further in Japanese Patent Application Laid-Open Nos. 144250/1980, 119132/1981 and 22437/1981, and German Patent No. 1,110,518, etc.), amino-substituted chalcone derivatives (described in the specification of US Patent No. 3,526,501, etc.), oxazole derivatives (described in the specification of US Patent No. 3,257,203, etc.), styrylanthracene derivatives (described in Japanese Patent Application Laid-Open No. 46234/1981, etc.), fluorenone derivatives (described in Japanese Patent No. 3,717,462, and in Japanese Patent Application Laid-Open Nos. 59143/1979, 52063/1980, 52064/1980, 46760/1980, 85495/1980, 11350/1982 and 148749/1982, etc.), and stilbene derivatives (described in Japanese Patent Application

Laid-Open Nos. 210363/1986, 228451/1986, 14642/1986, 72255/1986, 47646/1987, 36674/1987, 10652/1987, 30255/1987, 93445/1985, 94462/1985, 174749/1985, and 175052/1985, etc.)

[0061] Further, other examples thereof include silazane derivatives (described in the specification of US Patent No. 4950950), polysilane based material (described in Japanese Patent Application Laid-Open No. 204996/1990), aniline-based copolymer (described in Japanese Patent Application Laid-Open No. 282263/1990), and electrically conductive high molecular oligomer disclosed in the specification of Japanese Patent Application Laid-Open No. 211399/1989, among them, thiophene oligomer.

[0062] In the present invention, the above compounds can be used as a hole-injecting material, but it is preferred to use porphyrin compounds (described in Japanese Patent Application Laid-Open No. 2956965/1988, etc.), aromatic tertiary amine compounds or styrylamine compounds (described in the specification of US Patent No. 4,127,412, and Japanese Patent Application Laid-Open Nos. 27033/1978, 58445/1979, 149634/1979, 64299/1979, 79450/1980, 144250/1980, 119132/1981, 295558/1986, 98353/1986 and 295695/1988), and most preferably, said aromatic tertiary amine compounds are used.

[0063] Typical examples of the aforesaid porphyrin compounds are porphin; 1,10,15,20-tetraphenyl-21H,23H-por-

phin copper (II); 1,10,15,20-tetraphenyl-21H,23H-porphin zinc (II); 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphin; siliconphthalocyanine oxide, aluminum phthalocyanine chloride; phthalocyanine (nonmetal); dilithium phthalocyanine; copper tetramethylphthalocyanine; copper phthalocyanine; chrome phthalocyanine; zinc phthalocyanine; lead phthalocyanine; titanium phthalocyanine oxide; magnesium phthalocyanine; and copper octamethylphthalocyanine.

5 [0064] Typical examples of the aforesaid aromatic tertiary amine compounds or styrylamine compounds are N,N,N',N'-tetraphenyl-4,4'-diaminophenyl; N,N'-diphenyl-N,N'-di(3-methylphenyl)-4,4'-diaminobiphenyl; 2,2-bis(4-di-p-tolylaminophenyl)propane; 1,1-bis(4-di-p-tolylaminophenyl)cyclohexane; N,N,N',N'-tetra-p-tolyl-4,4'-diaminobiphenyl; 1,1-bis(4-di-p-tolylaminophenyl)-4-phenylcyclohexane; bis(4-dimethylamino-2-methylphenyl) phenylmethane; bis(4-di-p-tolylaminophenyl)phenylmethane; N,N'-diphenyl-N,N'-di(4-methoxyphenyl)-4,4'-diaminobiphenyl; N,N,N',N'-tetraphenyl-4,4'-diaminodiphenyl ether; 4,4'-bis(diphenylamino)quadrifphenyl; N,N,N-trip-tolyl)amine; 4-(di-p-tolylamino)-4'-(4-(di-p-tolylamino)styryl)stilbene; 4-N,N-diphenylamino-(2-diphenylvinyl)benzene; 3-methoxy-4'-N,N-diphenylaminostilbene; N-phenylcarbazole; and aromatic dimethylidine-based compounds.

10 [0065] The hole injecting layer in the EL device of the present invention can be obtained by forming the above compound into a film by the known method of film forming such as the vacuum deposition method, the spin coating method, or the LB method. The film thickness as said hole injecting layer is not particularly limited, but usually 5 nm to 5 μ m.

15 [0066] The hole injecting layer may consist of one layer comprising one or two or more of these hole-injecting materials, or may be a laminate of the aforesaid hole injecting layer and a hole injecting layer comprising other compound than the before-mentioned hole injecting layer.

20 [0067] As materials for the organic semiconductor layer, mention can be made of the following compounds.

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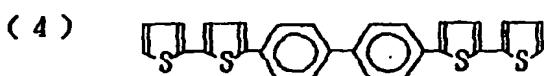
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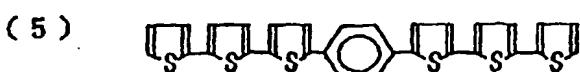
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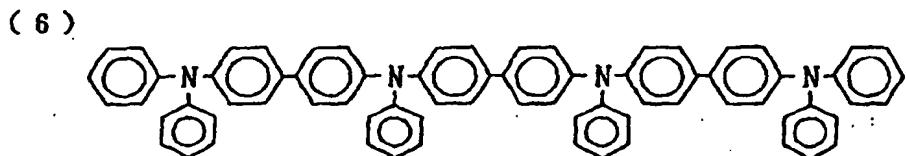
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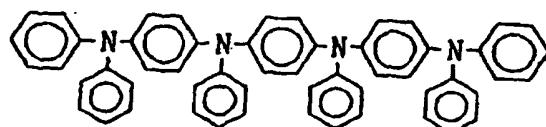
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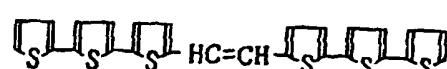
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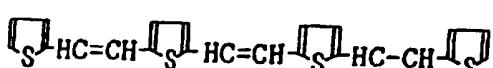
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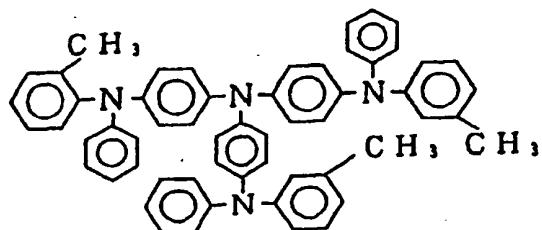
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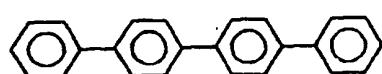
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[0068] As materials for the electron barrier layer, mention may be made of the following compounds.

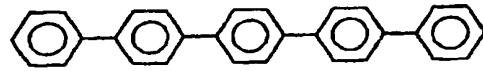
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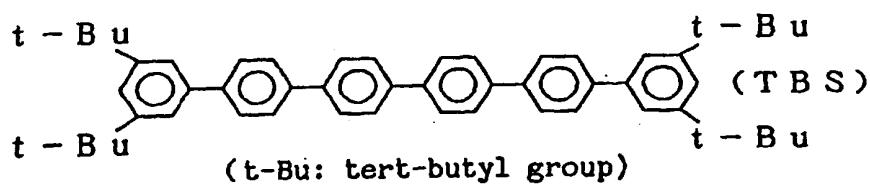
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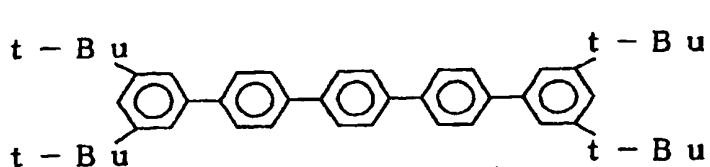
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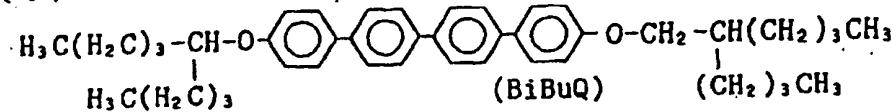
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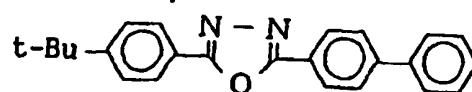
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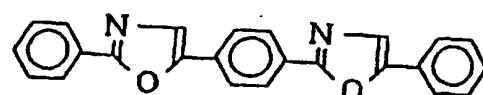
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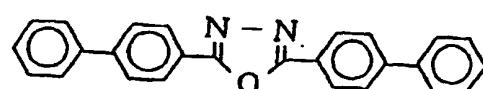
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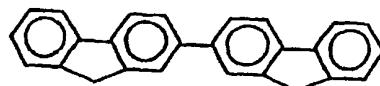
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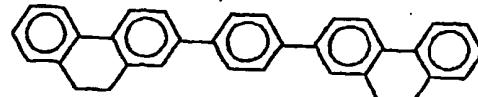
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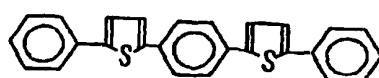
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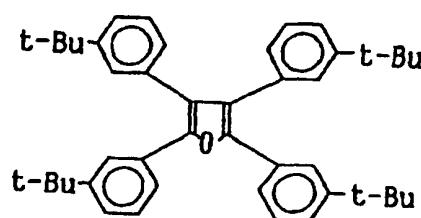
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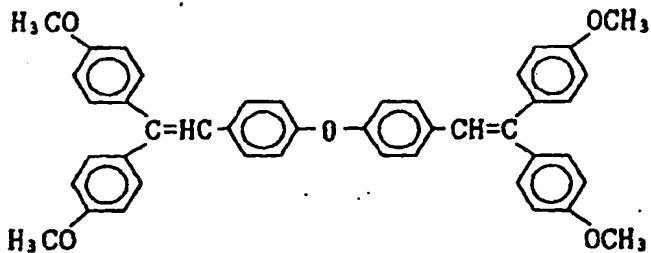
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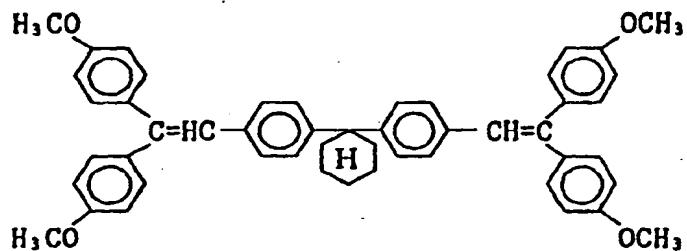


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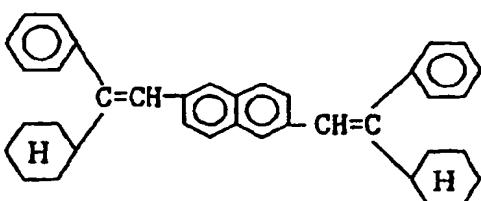
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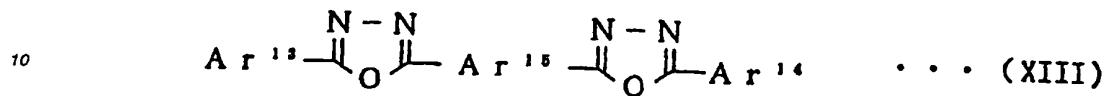


[0069] In addition, there may be used, between the light emitting layer and the cathode, an adhesive layer having excellent transmitting property for electron and favorable adhesivity to the cathode (electron injecting layer, adhesion improving layer).

[0070] An adhesive layer to be freshly added preferably contains a material having high adhesivity to both the light emitting layer and the cathode. Such material with high adhesivity thereto is exemplified by a metal complex of 8-hydroxyquinoline or derivative thereof, specifically a metal chelated oxinoide compound containing a chelate of oxine (generally, 8-quinolinol or 8-hydroxyquinoline).

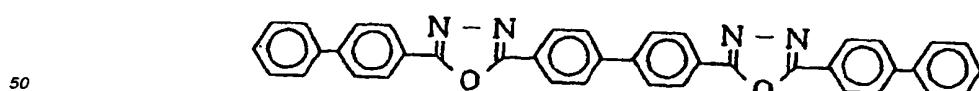
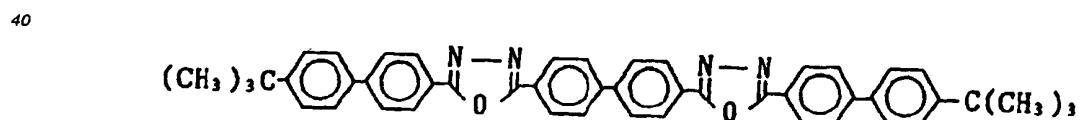
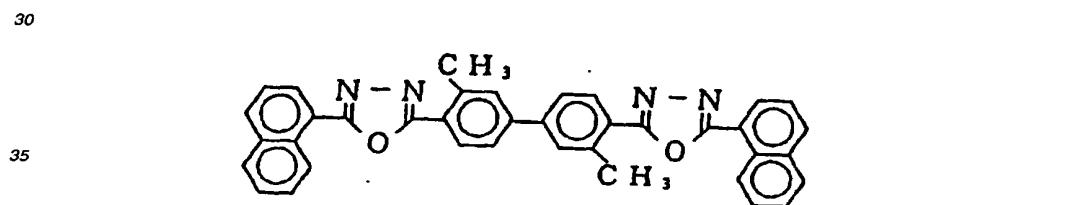
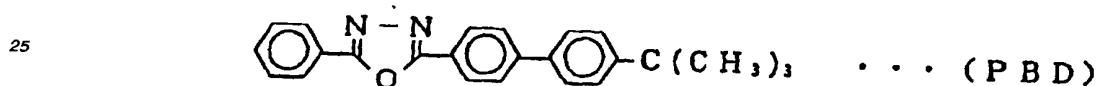
[0071] Moreover, there may be employed a layer comprising an oxadiazole derivative in place of the adhesive layer.

[0072] As the oxadiazole derivative, mention is made of an electron transmitting compound represented by any of the general formulae (XII) and (XIII).



15 wherein Ar¹¹ to Ar¹⁴ are each a substituted or unsubstituted aryl group, Ar¹¹ and Ar¹², and Ar¹³ and Ar¹⁴ may be each identical to or different from one another, and Ar¹⁵ is a substituted or unsubstituted arylene group. Examples of the aryl arylene group include a phenyl group, biphenyl group, anthracenyl group, perylenyl group and pyrenyl group. Examples of the aryl group and pyrenylene group. Examples of the substituent include an alkyl group having 1 to 10 carbon atoms, an alkoxyl group having 1 to 10 carbon atoms and a cyano group. The electron transmitting compound is preferably a thin-film forming compound.

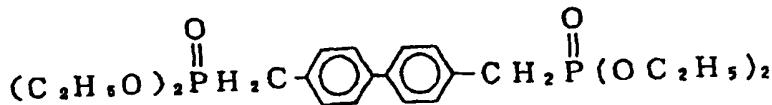
20 [0073] Specific examples of the above-mentioned electron transmitting compound include the following compound.



50 [0074] In the following, the present invention will be described in more detail with reference to synthesis examples and working examples, which however shall not be construed to limit the invention thereto.

55 Synthesis Example 1 (Synthesis of BCzVBi)

[0075] The phosphonic acid ester represented by the formula



in an amount of 1.8 g was dissolved in 20 ml of DMSO in an atmosphere of argon and 1.0 g of potassium-tert-butoxide (tBuOK) was added to the resultant solution. Thereafter 2.0 g of N-ethylcarbazole-3-carboxyaldehyde was added to the mixture with stirring at room temperature for 5 hours. [0076] To the resultant reaction mixture was added 100 ml of methanol, with the result that yellow powder precipitated. A solution of I₂ in benzene was added to the powder to recrystallize the same with the result that 0.8 g of yellow powder was obtained. The resultant product had a melting point of not lower than 300 °C. [0077] The determination results by proton nuclear magnetic resonance (¹H-NMR), infrared absorption (IR) spectrum and elemental analysis are given below.

(1) ¹H-NMR [solvent; CDCl₃, standard; tetramethylsilane (TMS)]

δ (ppm) = 6.9 to 8.5 (m, 26 H: central biphenylene ring/carb azole ring-H)
 δ (ppm) = 4.3 (q, 4H: ethyl-methylene (-CH₂-))
 δ (ppm) = 1.4 (t, 6H: ethyl-methyl (-CH₃))

(2) IR spectrum (KBr pellet method)

ν_{c=c} : 1600 cm⁻¹ (C = C stretching vibration)
 δ_{c-H} : 975 cm⁻¹ (C-H out-of-plane deformation vibration)

(3) Elemental analysis (The values in parentheses are theoretical values)

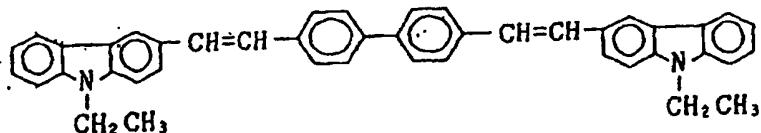
30

C	88.82 %	(89.15 %)
H	5.98 %	(6.12 %)
N	4.45 %	(4.73 %)

35 Molecular formula: C₄₄H₃₆N₂

[0078] It was confirmed from the above-mentioned determination results that the resultant compound was that represented by the formula

40



Synthesis Examples 2 to 8

50 [0079] Each compound was synthesized in the same manner as in Synthesis Example 1 except that any of the aldehydes, solvent, base and any of the phosphonic acid esters as shown in Table 1 were used.

55

Table 1

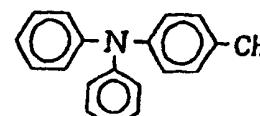
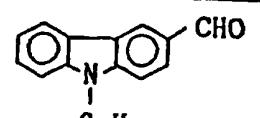
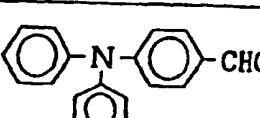
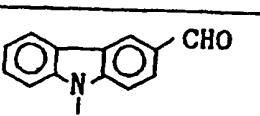
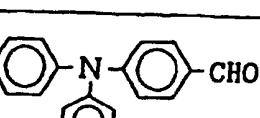
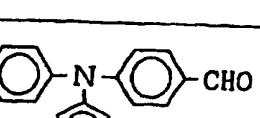
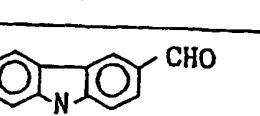
Synthesis Example	Species of chemical compound	Aldehyde	Solvent	Base
2	DPAVB _i		DMSO	t BuOK
3	BCzVB		DMSO	t BuOK
4	DPAVB _m		DMSO	t BuOK
5	BCzVBo		DMSO	t BuOK
6	DPAVBo		DMSO	t BuOK
7	DPAVB		DMSO	t BuOK
8	TCzVB		DMSO	t BuOK

Table 1 (continued)

Synthes- is Example	Phosphonic acid ester
2	$\text{O} \parallel \text{C}(\text{Ph}_2\text{P}(\text{OEt})_2)-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CH}_2\text{P}(\text{OEt})_2 \parallel \text{O}$
3	$\text{O} \parallel \text{C}(\text{Ph}_2\text{P}(\text{OEt})_2)-\text{C}_6\text{H}_4-\text{CH}_2\text{P}(\text{OEt})_2 \parallel \text{O}$
4	$\text{O} \parallel \text{C}(\text{Ph}_2\text{P}(\text{OEt})_2)-\text{C}_6\text{H}_5-\text{CH}_2\text{P}(\text{OEt})_2 \parallel \text{O}$
5	$\text{O} \parallel \text{C}(\text{Ph}_2\text{P}(\text{OEt})_2)-\text{C}_6\text{H}_5-\text{CH}_2\text{P}(\text{OEt})_2 \parallel \text{O}$
6	$\text{O} \parallel \text{C}(\text{Ph}_2\text{P}(\text{OEt})_2)-\text{C}_6\text{H}_5-\text{CH}_2\text{P}(\text{OEt})_2 \parallel \text{O}$
7	$\text{O} \parallel \text{C}(\text{Ph}_2\text{P}(\text{OEt})_2)-\text{C}_6\text{H}_4-\text{CH}_2\text{P}(\text{OEt})_2 \parallel \text{O}$
8	$\text{O} \parallel \text{C}(\text{Ph}_2\text{P}(\text{OEt})_2)-\text{C}_6\text{H}_4-\text{CH}_2\text{P}(\text{OEt})_2-\text{CH}_2\text{P}(\text{OEt})_2 \parallel \text{O}$

Synthesis Example 9

Synthesis of 1-(2-(4-methylphenyl)ethenyl)pyrene (MeSTPy)

[0080] 8.05 g (20 mmol) of 4-methylbenzyltriphenylphosphonium chloride and 4.61 g (20 mmol) of 1-pyrenecarboxy-

aldehyde were suspended in 150 ml of ethanol anhydride in an atmosphere of argon. Thereafter 40 ml (20 mmol) of 0.5 mole/liter solution of lithium ethoxide in ethanol was added dropwise to the resultant suspension at room temperature over a period of 30 minutes.

5 [0081] After the completion of the dropwise addition, stirring was carried out at room temperature for 30 minutes, and 20 ml of water was added to the suspension to arrest the reaction. The reaction product thus obtained was filtered and the residual cake was washed with methanol. The washed cake was recrystallized from cyclohexane containing a slight amount of iodine. As a result, yellow acicular crystal was obtained in an amount of 3.41 g (56 % yield).

10 [0082] The resultant product had a melting point of 155 to 156 °C

[0083] The determination results by proton nuclear magnetic resonance (¹H-NMR), IR spectrum and elemental analysis are given below.

(1) ¹H-NMR [solvent; CDCl₃, standard; tetramethylsilane (TMS)]

15 δ (ppm) = 2.40 (s, 3H; benzyl-methyl H)
 δ (ppm) = 7.2 to 8.6 (m, 15H; aromatic/ethenyl H)

(2) Elemental analysis (The values in parentheses are theoretical values)

C	94.73 %	(94.70 %)
H	5.28 %	(5.30 %)

Molecular formula: C₂₄H₁₆

25 [0084] It was confirmed from the above-mentioned determination result that the resultant compound was MeSTPy.

Synthesis Example 10

Synthesis of 1-(2-(4-(4-phenylethenyl)phenyl)ethenyl)pyrene (STSTPy)

30 [0085] 4.9 g (10 mmol) of 4-(2-phenylethenyl)benzyl triphenylphosphonium chloride and 2.30g (10 mmol) of 1-pyrenecarboxyaldehyde were suspended in 100 ml of ethanol anhydride in an atmosphere of argon. Thereafter 40 ml (20 mmol) of 0.5 mole/liter solution of lithium ethoxide in ethanol was added dropwise to the resultant suspension at room temperature over a period of 30 minutes.

35 [0086] After the completion of the dropwise addition, stirring was carried out at room temperature for 30 minutes, and 10 ml of water was added to the suspension to arrest the reaction. The reaction product thus obtained was filtered and the residual cake was washed with methanol. The washed cake was recrystallized from toluene containing a slight amount of iodine. As a result, yellow acicular crystal was obtained in an amount of 2.11 g (52 % yield).

40 [0087] The resultant product had a melting point of 259 to 260°C.

[0088] The determination results by proton nuclear magnetic resonance (¹H-NMR), IR spectrum and elemental analysis are given below.

(1) ¹H-NMR [solvent; deuterated dimethyl sulfoxide (DMSO-d6). standard; tetramethylsilane (TMS), 100°C]

45 δ (ppm) = 7.2 to 8.4 (m, 22 H; aromatic/ethenyl H)

(2) Elemental analysis (The values in parentheses are theoretical values)

C	94.58 %	(94.55 %)
H	5.41 %	(5.45 %)

Molecular formula: C₃₂H₂₂

55 [0089] It was confirmed from the above-mentioned determination result that the resultant compound was STSTPy.

Synthesis Example 11

Synthesis of 9-(2-phenylethenyl)anthracene (STA)

5 [0090] 3.89 g (10 mmol) of benzyltriphenylphosphonium chloride and 2.06 g (10 mmol) of 9-anthracenecarboxyaldehyde were suspended in 100 ml of ethanol anhydride in an atmosphere of argon. Thereafter 20 ml (10 mmol) of 0.5 mole/liter solution of lithium ethoxide in ethanol was added dropwise to the resultant suspension at room temperature over a period of 30 minutes.

10 [0091] After the completion of the dropwise addition, stirring was carried out at room temperature for 30 minutes, and 10 ml of water was added to the suspension to arrest the reaction. The reaction product thus obtained was filtered and the residual cake was washed with methanol. The washed cake was recrystallized from cyclohexane containing a slight amount of iodine. As a result, yellow acicular crystal was obtained in an amount of 3.41 g (48 % yield).

15 [0092] The resultant product had a melting point of 132 to 133°C.

[0093] The determination results by proton nuclear magnetic resonance (¹H-NMR), IR spectrum and elemental analysis are given below.

(1) ¹H-NMR [solvent; CDCl₃, standard; tetramethylsilane (TMS)]

δ (ppm) = 6.8 to 8.2 (m, 16 H; aromatic/ethenyl H)

20 (2) Elemental analysis (The values in parentheses are theoretical values)

C	94.28 %	(94.25 %)
H	5.70 %	(5.75 %)

25

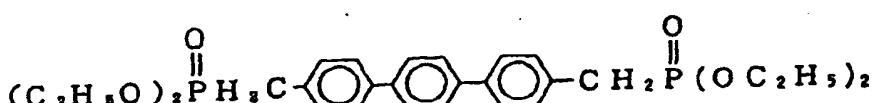
Molecular formula: C₂₂H₁₆

[0094] It was confirmed from the above-mentioned determination result that the resultant compound was STA.

Synthesis Example 12 (Synthesis of DPAVTP)

30 [0095] The phosphonic acid ester represented by the formula

35



40

in an amount of 1.86 g and 2.5 g of 4-(N,N-diphenylamino) benzaldehyde were dissolved in 30 ml of DMSO in an atmosphere of argon and 0.9 g of potassium-tert-butoxide (t-BuOK) was added to the resultant solution to proceed with reaction at room temperature for 4 hours. The resultant product was allowed to stand overnight.

45

[0096] To the resultant reaction mixture was added 50 ml of methanol with the result that yellow powder precipitated.

[0097] The determination results by proton nuclear magnetic resonance (¹H-NMR), mass spectrometry and elemental analysis are given below.

50

(1) ¹H-NMR [solvent; CDCl₃, standard; tetramethylsilane (TMS)]

δ (ppm) = 6.9 to 7.6 (m, 44 H; central terphenylene ring/vinyl CH=CH/and triphenylamine ring-H)

55

(2) Mass spectrometry (FD-MS)

Only m/z = 768 (z=1) and m/z=384 (z=2) were obtained against C₅₈H₄₄N₂=768

(3) Elemental analysis (The values in parentheses are theoretical values)

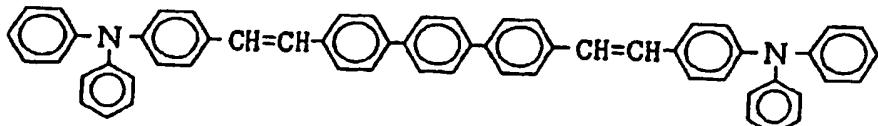
C	90.72 %	(90.59 %)
H	5.57 %	(5.77 %)
N	3.71 %	(3.64 %)

5

[0098] It was confirmed from the above-mentioned determination result that the resultant compound was that represented by the formula

10

15



20

[0099] Indium tin oxide (ITO) was provided on a 25 mm x 75 mm x 1.1 mm glass substrate (NA40, produced by HOYA Corporation) in a 100 nm thick film by vapor deposition method to obtain a transparent supporting substrate (produced by HOYA Corporation).

[0100] The substrate had been ultrasonically washed in isopropyl alcohol for 5 minutes, dried by blowing nitrogen and, then subjected to UV ozone washing for 10 minutes in an apparatus (UV 300; manufactured by Samco International Institute Inc.). A substrate holder of a commercially available vapor deposition system (manufactured by ULVAC Co., Ltd.) was fixed onto the transparent supporting substrate. Then 200 mg of N,N'-bis(3-methylphenyl)-N,N'-diphenyl[1,1'-biphenyl]-4,4'-diamine(TPD) was placed in an electrically-heated boat made of molybdenum, 200 mg of 4,4'-bis(2,2-diphenylvinyl)biphenyl (DPVBi) was placed in another electrically heated boat made of molybdenum, further 200 mg of the compound (A) (shown in Table 2) as the charge injection auxiliary material was placed in another electrically heated boat made of molybdenum, and the vacuum chamber was depressurized to 1×10^{-4} Pa. After that, the boat containing TPD was heated to 215 to 220°C, and TPD was vapor-deposited on the transparent supporting substrate at a vapor deposition rate of 0.1 to 0.3 nm/sec to obtain a positive hole injection layer of 60 nm in film thickness. In this vapor deposition process, the substrate was at room temperature.

[0101] Without taking the substrate out of the vacuum chamber, DPVBi was laminated in a thickness of 40 nm on the positive hole injection layer and simultaneously, the boat containing the compound (A) was heated to mix the compound (A) in the light emitting layer. As to the vapor deposition rate, the deposition rate of the compound (A) was set to the values in column (C) in Table 2 against the deposition rate of DPVBi in column (B) in Table 2. Therefore, the mixing ratio (ratio of the compound (A) to the host material) was set to the values in column (D) in Table 2.

[0102] Subsequently, the pressure in the vacuum chamber was raised to the atmospheric pressure, an aluminum complex of 8-hydroxyquinoline as the material of the adhesive layer was newly placed in an electrically-heated boat made of molybdenum, 1 g of magnesium ribbon was placed in an electrically heated boat made of molybdenum, and 500 mg of silver wire was placed in a tungsten basket. The pressure of vacuum chamber was reduced to 1×10^{-4} Pa. Then, the aluminum complex of 8-hydroxyquinoline was vapor-deposited at a vapor deposition rate of 0.01 to 0.03 nm/sec to form an adhesive layer with a film thickness of 20 nm. In addition, silver and magnesium were simultaneously vapor-deposited at vapor deposition rate of 0.1 nm/sec and 1.4 nm/sec, respectively to form the cathode composed of the mixed electrode of silver and magnesium with a film thickness of 150 nm.

[0103] A voltage of 7 V was applied to the device thus obtained, and measurements were made of the current density and the brightness of the device to calculate the luminous efficiency of the same. The results are given in Table 2.

50

55

Table 2

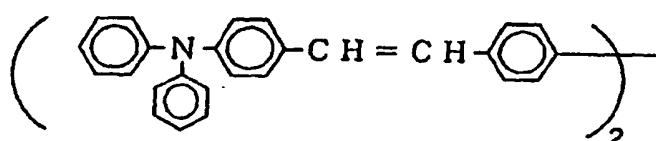
	(A)	(B) (nm/sec)	(C) (nm/sec)	(D) Mixing ratio (% by wei- ght)
Example 1	DPAVB1	2.8 ~ 3.0	0.1 ~ 0.13	3 ~ 4
Example 2	BCzVB	3.5 ~ 4.5	0.02	0.6 ~ 0.4
Example 3	BCzVB1	3.0 ~ 4.0	0.7	1.5 ~ 1.9
Example 4	DPAVBm	2.7 ~ 3.7	0.1 ~ 0.13	3 ~ 5
Example 5	BCzVBo	2.7 ~ 3.7	0.1 ~ 0.13	3 ~ 5
Example 6	DPAVBo	3.0 ~ 4.5	0.04	0.9 ~ 1.3
Example 7	DPAVB	3.0 ~ 4.0	0.05	1.2 ~ 1.6
Example 8	TCzVB	2.5 ~ 3.0	0.05 ~ 0.07	1.6 ~ 2.7
Comparative Example 1	none	2	none	0

Table 2 (continued)

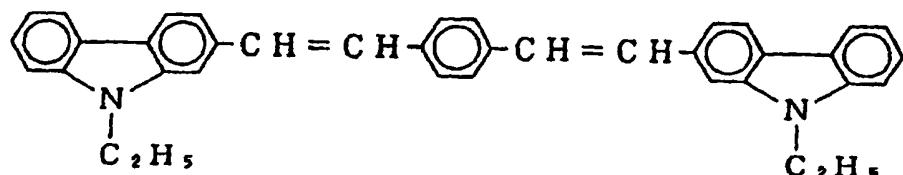
	Current density (mA/cm ²)	Brightness (cd/m ²)	Luminous efficiency (lm/w)	Luminous color
Example 1	15.0	230	0.7	bluish green
Example 2	7.5	200	1.2	blue
Example 3	9.5	162	0.8	blue
Example 4	9.0	164	0.8	blue
Example 5	11.0	130	0.5	blue
Example 6	11.4	220	0.9	blue
Example 7	7.5	210	1.3	greenish blue
Example 8	7.0	160	1.0	blue
Comparative Example 1	0.7	10	0.6	blue

Remarks: The abbreviated compounds (A) are detailed as follows

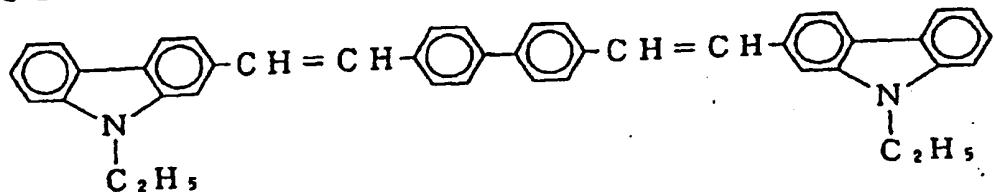
D P A V B I :



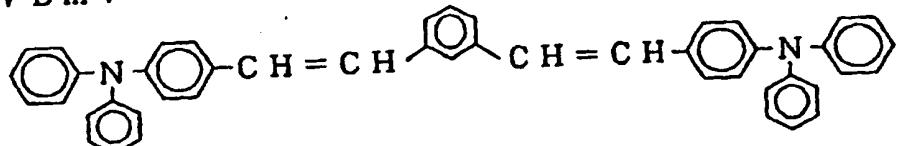
B C z V B :



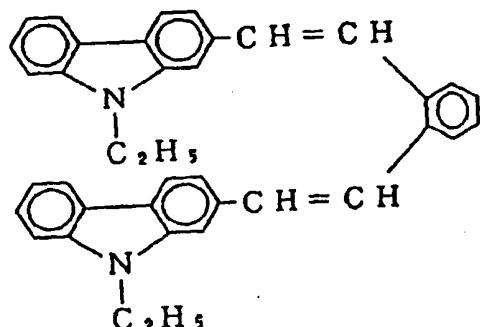
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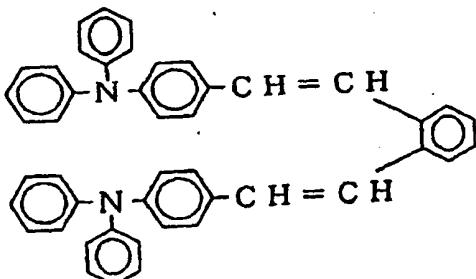
D P A V B m :



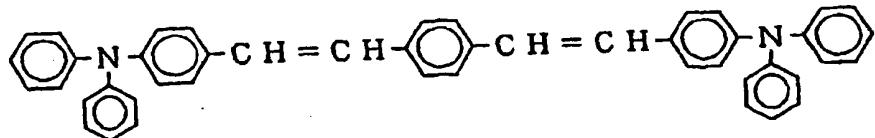
D C z V B o :



D P A V B o :



D P A V B :



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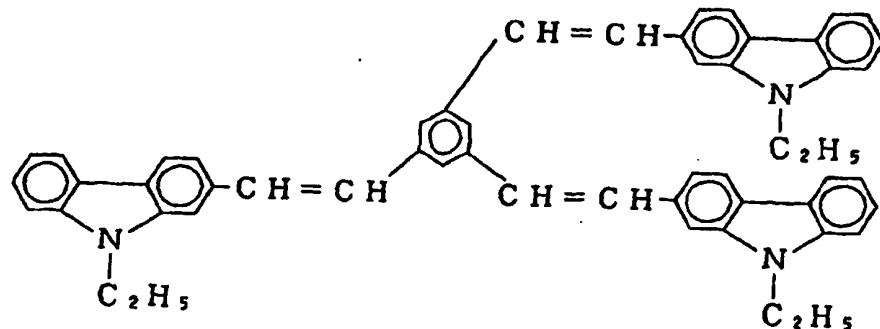
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T C z V B :

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[0104] As can be seen from Table 2, the examples having the compound (A) mixed therein are increased in the amount of current flow in terms of current density and is improved in charge injection properties, which leads without fail to a decrease in voltage required to be applied to the device.

Comparative Example 1

[0105] The procedure in Example 1 was repeated to prepare the device except that the use of the compound (A) was omitted.

[0106] The device thus obtained had a single luminous peak wavelength of 472 nm.

Example 9

[0107] The procedure in Example 1 was repeated to prepare the device except that DPAVBi as the compound (A) was incorporated in DPVBi in an amount of 3 % by weight, the film thickness of the light emitting layer (mixed layer of DPAVBi and DPVBi) was set at 55 nm, and the film thickness of the positive hole injecting layer was set at 45 nm.

[0108] A voltage of 8 V was applied to the device thus obtained, with the results that there was obtained a light emission having a current density of 7 mA/cm², brightness of 400 cd/m² and peak wavelength of 494 nm. The resultant light emission constituted the spectrum having three peaks at 462 nm, 494 nm and 534 nm, which demonstrates that DPAVBi emits light. The luminous efficiency thereof was 2.2 lumen/W and was surpassingly excellent as compared with that of the comparative example. It is also pointed out that the charge injection auxiliary material exhibits fluorescent doping effect as the case may be.

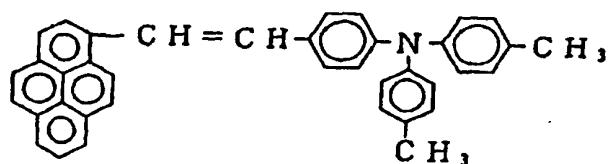
Example 10

[0109] The procedure in Example 1 was repeated to prepare the device except that the aluminum complex of 8-hydroxyquinoline was used as the light emitting material, STP was used as the charge injection auxiliary material, the mixing ratio thereof was set at 0.7 % by weight and the film thickness of the light emitting layer was set at 40 nm. A voltage of 5.5 V was applied to the device thus obtained, with the result that there was obtained a green light emission having a current density of 23 mA/cm² and brightness of 1000 cd/m². The luminous efficiency thereof was 2.4 lumen/W.

50

S T P :

55



Comparative Example 2

[0110] The procedure in Example 1 was repeated to prepare the device except that the aluminum complex of 8-hydroxyquinoline was used as the light emitting material and the use of the compound (A) was omitted.

[0111] A voltage of 7 V was applied to the device thus obtained, with the result that there was obtained a green light emission having a current density of 23 mA/cm² and brightness of 780 cd/m². The luminous efficiency thereof was 1.5 lumen/W.

Comparative Example 3

[0112] The procedure in Example 1 was repeated to prepare the device except that DPVBi was used as the host material, 3-(2'-benzothiazolyl)-7-diethylamino-coumarin (KU 7: Japanese Patent Application Laid-Open No. 264692/1988) was used in place of the charge injection auxiliary material, and the mixing ratio thereof was set at 2 % by weight.

[0113] A voltage of 7 V was applied to the device thus obtained, with the result that there was obtained a green light emission having a current density of 5 mA/cm² and brightness of 150 Cd/m².

[0114] It is understood by the result of comparing Comparative Examples 2 and 3 with Example 10 that the device comprising the charge injection auxiliary material according to the present invention attains a decrease in voltage required to be applied to the device as well as an enhancement in luminous efficiency.

[0115] In addition, the device containing coumarin 7 (KU 7) as the dopant causes the applied charge to increase.

Examples 11 to 13

[0116] The procedures in Examples 1 to 8 were repeated to prepare the devices except that UV washing was carried out for 30 minutes. A voltage of 7 V was applied to the device thus obtained, and measurements were made of the current density and the brightness of the device to calculate luminous efficiency of the same. The results obtained are given in Table 3.

Table 3

	(A)	(B) (nm/sec)	(C) (nm/sec)	(D) Mixing ratio (% by weight)
Example 11	STSTPy	2.5 ~ 3.2	0.1 ~ 0.12	3.2 approx.
Example 12	MeSTPy	2.7 ~ 3.7	0.1 ~ 0.12	3.2 approx.
Example 13	STPy	3.0 ~ 3.5	0.06	2 approx.

Table 3 (continued)

	Current density (mA/cm ²)	Brightness (cd/m ²)	Luminous efficiency (lm/W)	Luminous color
Example 11	7.0	101	0.65	bluish green
Example 12	6.0	120	0.9	blue
Example 13	8.0	110	0.62	blue

Reference Example 1

[0117] An initial DC voltage of 6.94 V was applied to the device as obtained in Example 11 to make the device continuously emit light under a constant current condition. The brightness after 200 hours of continuous driving maintained 85 % of the initial brightness, thus exhibiting an extremely stable light emission.

[0118] The increase in the driving voltage was only one (1) V.

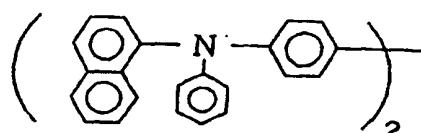
[0119] On the other hand, the device as obtained in Comparative Example 1 was made to continuously emit light under the condition same as above with the result that the brightness after 200 hours of continuous driving decreased to one half, that is, 50 % of the initial brightness.

Examples 14 to 16

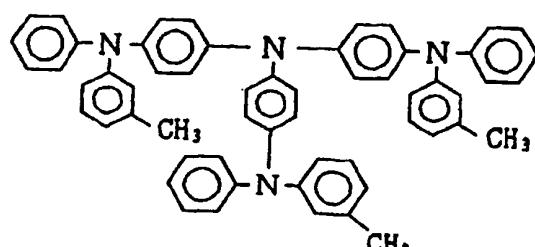
[0120] The procedures in Examples 1 to 8 were repeated to prepare the devices except that for the positive hole injecting layer, CuPc (lamine constitution of copper phthalocyanine/NPD with film thickness of 20 nm/ 40nm) was used in Example 14, and MTDATA/ NPD with film thickness of 60 nm/ 20nm which is a kind of semiconductor oligomer was used in Examples 15 and 16.

[0121] NPD: [N,N-bis(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine]

20



M T D A T A :



[0122] A voltage of 7 V was applied to the device thus obtained, and measurements were made of the current density and the brightness of the device to calculate luminous efficiency of the same. The results are given in Table 4.

[0123] The charge injection auxiliary material as used in any of Examples 14 to 16 functioned as the fluorescent dopant and had an energy gap less than that in the light emitting layer. The energy gap in a light emitting layer is determined by the energy value at the light absorption end of the vapor-deposited film, while that in a charge injection auxiliary material is determined by the energy value at the light absorption edge of a dilute solution from a solvent having a low dielectric constant (for example, toluene and a halogenous solvent).

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Table 4

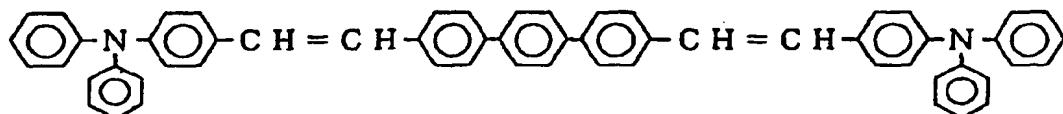
	(A)	(B) (nm/sec)	(C) (nm/sec)	(D) Mixing ratio (% by weight)
Example 14	DPAVBi	2.7 ~ 3.0	0.1 2	3.8 ~ 4.2
Example 15	DPAVTP	2.5 ~ 3.0	0.0 9	2.9 ~ 3.4
Example 16	DPAVB	3.0 ~ 5.0	0.0 9	1.8 ~ 2.9

Table 4 (continued)

	Current density (mA/cm ²)	Brightness (cd/m ²)	Luminous efficiency (lm/W)	Luminous color
Example 14	21.6	540	1.3	greenish blue
Example 15	7.1	111	0.64	blue
Example 16	2.58	160	2.8	bluish green

Remark: The abbreviated compound (A) are detailed as follows
DPAVBi, DPAVB; as previously defined.

DPAVTP



[0124] As can be seen from Table 4 and as compared with Comparative Example 1, any of the devices in these examples attains improvement in charge injection properties, decrease in voltage required to be applied and enhancement in efficiency.

Examples 17 and 18

[0125] To any of the devices as obtained in Examples 14 and 15, an initial voltage as shown in Table 5 was applied in an atmosphere of dry nitrogen to carry out continuous driving under a constant current condition. As a result, half-lives as shown in Table 5 were obtained, thus achieving prolonged service life. The prolonged service life is observed in a charge injection auxiliary material having in particular, an energy gap less than that in the light emitting layer. Table 5 gives the energy gap along with the ionization energy in the charge injection auxiliary material. The initial brightness was 100 cd/m², and the light emitting layer had an energy gap of 2.97 eV.

Table 5

	Initial voltage (V)	Voltage on reduction to half (V)	Half life (hr)	Charge injection auxiliary material	
				Energy gap (eV)	Ionization energy (eV)
Example 17	6.2	7.8	1000	2.8 4	5.6
Example 18	7.1	9.0	610	2.8 7	5.6

[0126] As can be seen from Table 5, the devices are low in voltage increase. The conventional devices usually bring about increase in driving voltage of 3 to 4 V with the elapse of time, whereas the devices in Examples 17 and 18 showed lessened increase in driving voltage of 1.6 V and 1.9 V, respectively, thereby demonstrating excellent stability

INDUSTRIAL AVAILABILITY

[0127] The charge injection auxiliary material according to the present invention is capable of effectively enhancing charge injection properties and hence is well suited for use in various organic electronic devices such as electrophotographic photoreceptor and organic EL device.

[0128] In addition, the organic EL device comprising the above-mentioned charge injection auxiliary material according to the present invention is characterized by a lower applied-voltage, an enhanced light emission efficiency and a prolonged service life.

Claims

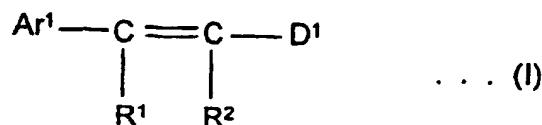
30 1. A functional layer of an organic electron device, comprising a positive-hole transporting organic host substance which is subjected to a positive-hole injection from an external layer and has enhanced positive-hole injection properties by incorporation of a charge injection auxiliary material consisting of a stilbene derivative, a distyrylarylene derivative or a tris(styrylarylene) derivative, said charge injection auxiliary material being in an amount of 19 % by weight or less, preferably 0.05 to 9 % by weight based on the weight of the positive-hole transporting organic host substance.

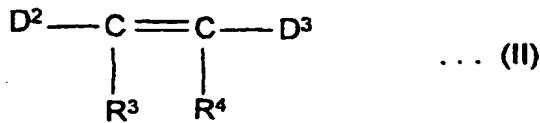
35 2. The functional layer according to claim 1, wherein the functional layer is a light emitting layer, a positive-hole injecting layer, a positive-hole transporting layer or an electron barrier layer.

36 3. The functional layer according to claim 1 or 2, wherein the stilbene derivative, the distyrylarylene derivative or the tris(styrylarylene) derivative has at least one electron donating group.

40 4. The functional layer according to claim 3, wherein the electron donating group is selected from an alkoxy group having 1 to 10 carbon atoms, an aryloxy group having 6 to 20 carbon atoms or an amino group with a hydrocarbon radical having 1 to 30 carbon atoms.

45 5. The functional layer according to any one of claims 1 to 4, wherein the stilbene derivative is a compound represented by the general formula (I) or (II):

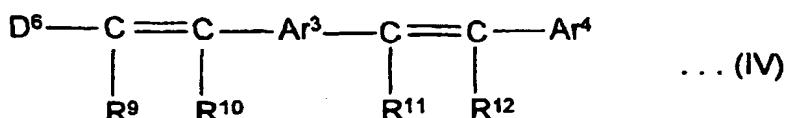
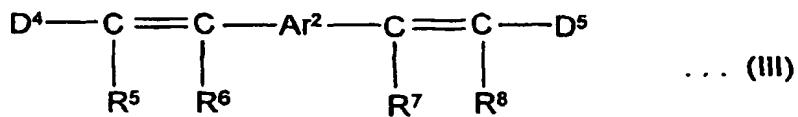




10 wherein Ar^1 is an aryl group having 6 to 20 carbon atoms, a thienyl group or a bithienyl group, R^1 to R^4 are each a hydrogen atom, an aryl group having 6 to 20 carbon atoms, a thienyl group or a bithienyl group, R^1 and R^2 , and R^3 and R^4 may be each the same or different, respectively, D^1 to D^3 are each an aryl group having 6 to 20 carbon atoms which is substituted with an electron donating group, a thienyl group, a bithienyl group or a condensed polycyclic group having 10 to 30 carbon atoms, D^2 and D^3 may be the same or different, and Ar^1 and R^1 to R^4 may be each unsubstituted or substituted with an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, an arylalkyl group having 7 to 10 carbon atoms or an amino group with a hydrocarbon radical having 1 to 20 carbon atoms.

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20 6. The functional layer according to any one of claims 1 to 4, wherein the distyrylarylene derivative is a compound represented by the general formula (III) or (IV):



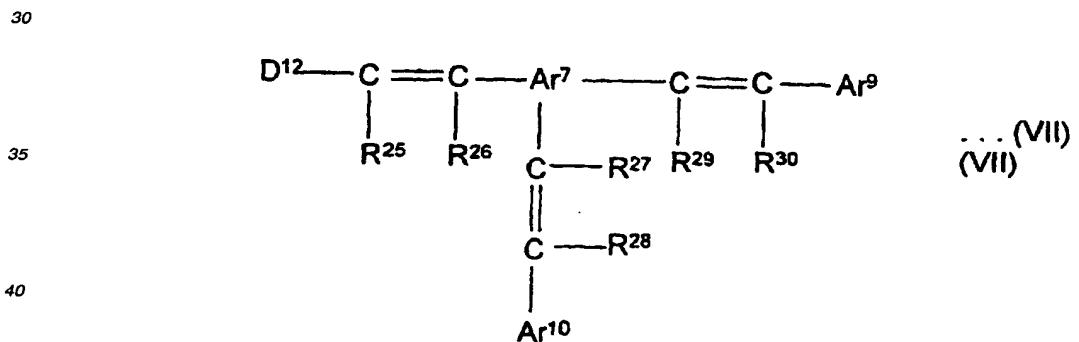
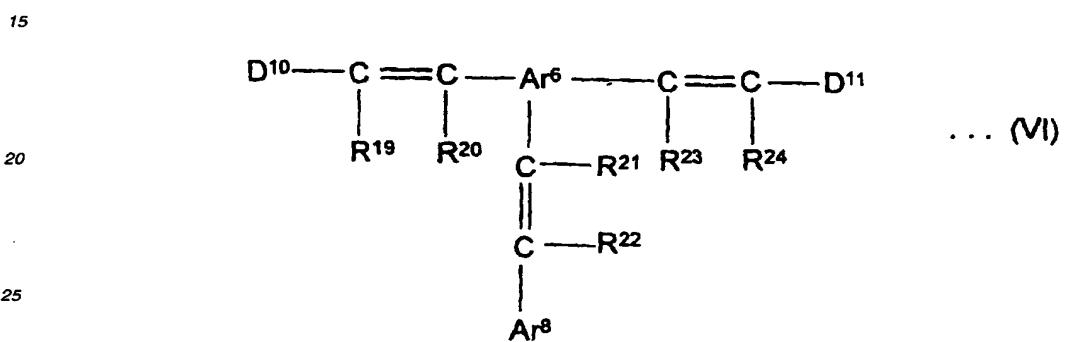
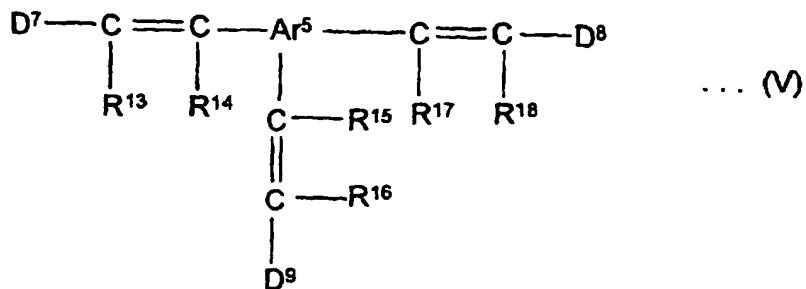
35 wherein Ar^2 and Ar^3 are each an arylene group having 6 to 20 carbon atoms, a thienylene group or a bithienylene group, Ar^4 is an aryl group having 6 to 20 carbon atoms, a thienyl group or a bithienyl group, R^5 to R^{12} are each a hydrogen atom, an aryl group having 6 to 20 carbon atoms, a thienyl group or a bithienyl group, R^5 to R^8 ; and R^9 to R^{12} may be each the same or different, respectively, D^4 to D^6 are each an aryl group having 6 to 20 carbon atoms which is substituted with an electron donating group, a thienyl group, a bithienyl group or a condensed polycyclic group having 10 to 30 carbon atoms, D^4 and D^5 may be the same or different, and Ar^2 to Ar^4 and R^5 to R^{12} may each be unsubstituted or substituted with an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, an arylalkyl group having 7 to 10 carbon atoms or an amino group with a hydrocarbon radical having 1 to 20 carbon atoms.

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45 7. The functional layer according to any one of claims 1 to 4, wherein the tris(styrylarylene) derivative is a compound represented by the general formula (V), (VI) or (VII):

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45 wherein Ar^5 to Ar^7 are each a trivalent aromatic ring radical having 6 to 24 carbon atoms, Ar^8 to Ar^{10} are each an aryl group having 6 to 20 carbon atoms, a thiienyl group or a bithienyl group, Ar^9 and Ar^{10} may be the same or different, R^{13} to R^{30} are each a hydrogen atom, an aryl group having 6 to 20 carbon atoms, a thiienyl group or a bithienyl group, R^{13} to R^{18} ; and R^{19} to R^{24} ; and R^{25} to R^{30} may be each the same or different, respectively, D^7 to D^{12} are each an aryl group having 6 to 20 carbon atoms which is substituted with an electron donating group, a thiienyl group, a bithienyl group or a condensed polycyclic group having 10 to 30 carbon atoms, D^7 to D^9 , D^{10} and D^{11} may be same or different, and Ar^5 to Ar^{10} and R^{13} to R^{30} may be each unsubstituted or substituted with an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, an aryloxy group having 6 to 10 carbon atoms; an arylalkyl group having 7 to 10 carbon atoms or an amino group with a hydrocarbon radical having 1 to 20 carbon atoms.

50 55 8. The functional layer according to any one of claims 3 to 7, wherein the charge injection auxiliary material has at least one of the electron donating group and the condensed polycyclic group so as to function also as a fluorescent dopant.

9. An organic electron device comprising the functional layer according to any one of claims 1 to 8 and an external layer.

10. The organic electron device according to claim 9, being an organic electroluminescence device.

5 11. The electroluminescence device according to claim 10, wherein the functional layer is the light emitting layer.

12. The electroluminescence device according to claim 11, wherein the ionization energy of the charge injection auxiliary material is smaller than the ionization energy of the light emitting layer.

10 13. The electroluminescence device according to claim 11 or 12, wherein the energy gap of said charge injection auxiliary material is smaller than the energy gap of the light emitting layer.

14. The electroluminescence device according to any one of Claims 11 to 13, wherein the charge injection auxiliary material is excited by the recombination of positive holes and electrons in the light emitting layer whereby said material emits light.

15 15. The electroluminescence device according to any one of Claims 11 to 14, wherein the energy gap of the charge injection auxiliary material is smaller than the energy gap of the light emitting layer by at least 0.1 eV.

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Patentansprüche

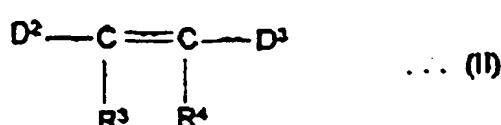
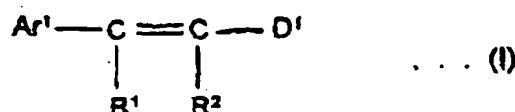
1. Funktionelle Schicht einer organischen Elektronenvorrichtung, umfassend eine organische Wirtssubstanz zum Transport positiver Löcher, die einer Injektion positiver Löcher von einer Außenschicht unterworfen wird und verbesserte Injektionseigenschaften positiver Löcher durch Einbringung eines Ladungsinjektions-Hilfsmaterials, bestehend aus einem Stilbenderivat, einem Distyrylarylenderivat oder einem Tris(styrylarylen)derivat, besitzt, wobei das Ladungsinjektionsmaterial in einer Menge von 19 Gew.-% oder weniger, vorzugsweise von 0,05 bis 9 Gew.-%, auf Basis des Gewichts der organischen Wirtssubstanz zum Transport positiver Löcher vorliegt.

25 2. Funktionelle Schicht nach Anspruch 1, wobei die funktionelle Schicht eine lichtemittierende Schicht, eine Injektionsschicht positiver Löcher, eine Transportschicht positiver Löcher oder eine Elektronensperrschicht ist.

30 3. Funktionelle Schicht nach Anspruch 1 oder 2, wobei das Stilbenderivat, das Distyrylarylenderivat oder das Tris(styrylarylen)derivat mindestens eine elektronenabgebende Gruppe aufweist.

35 4. Funktionelle Schicht nach Anspruch 3, wobei die elektronenabgebende Gruppe gewählt ist aus einer Alkoxygruppe mit 1 bis 10 Kohlenstoffatomen, einer Aryloxygruppe mit 6 bis 20 Kohlenstoffatomen oder einer Aminogruppe mit einem Kohlenwasserstoffrest mit 1 bis 30 Kohlenstoffatomen.

40 5. Funktionelle Schicht nach mindestens einem der Ansprüche 1 bis 4, wobei das Stilbenderivat eine durch die allgemeine Formel (I) oder (II) angegebene Verbindung ist:



worin Ar^1 eine Arylgruppe mit 6 bis 20 Kohlenstoffatomen, eine Thienylgruppe oder eine Bithienylgruppe ist, R^1 bis R^4 jeweils ein Wasserstoffatom, eine Arylgruppe mit 6 bis 20 Kohlenstoffatomen, eine Thienylgruppe oder eine Bithienylgruppe sind, R^1 und R^2 bzw. R^3 und R^4 jeweils dasselbe oder verschieden sein können, D^1 bis D^3 jeweils eine Arylgruppe mit 6 bis 20 Kohlenstoffatomen sind, welche durch eine elektronenabgebende Gruppe, eine Thienylgruppe, eine Bithienylgruppe oder eine kondensierte polycyclische Gruppe mit 10 bis 30 Kohlenstoffatomen substituiert ist, D^2 und D^3 dasselbe oder verschieden sein können und Ar^1 und R^1 bis R^4 jeweils unsubstituiert oder substituiert sein können mit einer Alkylgruppe mit 1 bis 10 Kohlenstoffatomen, einer Alkoxygruppe mit 1 bis 10 Kohlenstoffatomen, einer Aryloxygruppe mit 6 bis 10 Kohlenstoffatomen, einer Arylalkylgruppe mit 7 bis 10 Kohlenstoffatomen oder einer Aminogruppe mit einem Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen.

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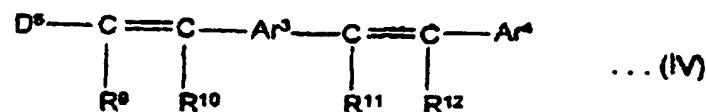
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6. Funktionelle Schicht nach mindestens einem der Ansprüche 1 bis 4, wobei das Distyrylarylenderivat eine durch die allgemeine Formel (III) oder (IV) angegebene Verbindung ist:

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worin Ar^2 und Ar^3 jeweils eine Arylengruppe mit 6 bis 20 Kohlenstoffatomen, eine Thienylgruppe oder eine Bithienylgruppe sind, Ar^4 eine Arylgruppe mit 6 bis 20 Kohlenstoffatomen, eine Thienylgruppe oder eine Bithienylgruppe ist, R^5 bis R^{12} jeweils ein Wasserstoffatom, eine Arylgruppe mit 6 bis 20 Kohlenstoffatomen, eine Thienylgruppe oder eine Bithienylgruppe sind, R^5 bis R^8 bzw. R^9 bis R^{12} jeweils dasselbe oder verschieden sein können, D^4 bis D^6 jeweils eine Arylgruppe mit 6 bis 20 Kohlenstoffatomen sind, welche mit einer elektronenabgebenden Gruppe, einer Thienylgruppe, einer Bithienylgruppe oder einer kondensierten polycyclischen Gruppe mit 10 bis 30 Kohlenstoffatomen substituiert ist, D^4 und D^5 dasselbe oder verschieden sein können und Ar^2 bis Ar^4 und R^5 bis R^{12} jeweils unsubstituiert oder substituiert sein können mit einer Alkylgruppe mit 1 bis 10 Kohlenstoffatomen, einer Alkoxygruppe mit 1 bis 10 Kohlenstoffatomen, einer Aryloxygruppe mit 6 bis 10 Kohlenstoffatomen, einer Arylalkylgruppe mit 7 bis 10 Kohlenstoffatomen oder einer Aminogruppe mit einem Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen.

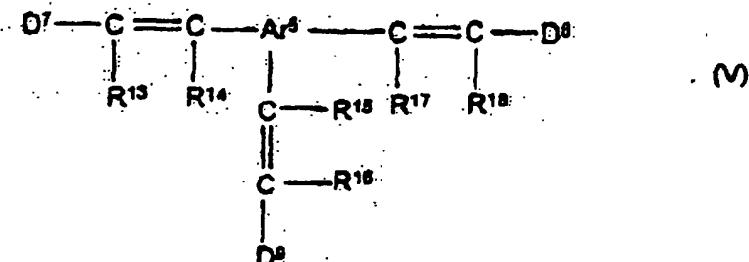
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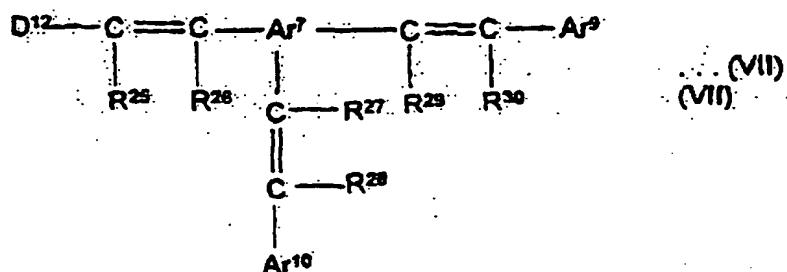
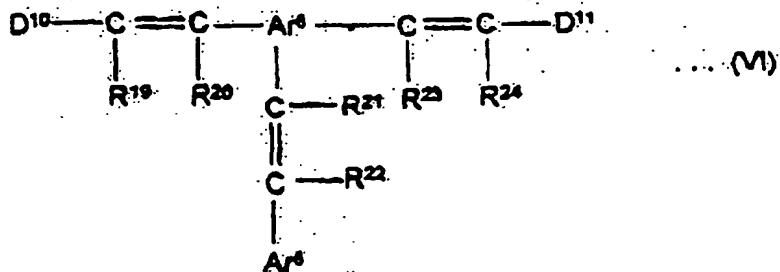
7. Funktionelle Schicht nach mindestens einem der Ansprüche 1 bis 4, wobei Tris(styrylarylen)-derivat eine Verbindung ist, angegeben durch die allgemeine Formel (V), (VI) oder (VII):

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worin Ar⁵ bis Ar⁷ jeweils ein dreiwertiger aromatischer Ringrest mit 6 bis 24 Kohlenstoffatomen sind, Ar⁸ bis Ar¹⁰ jeweils eine Arylgruppe mit 6 bis 20 Kohlenstoffatomen, eine Thienylgruppe oder eine Bithienylgruppe sind, Ar⁹ und Ar¹⁰ dasselbe oder verschieden sein können, R¹³ bis R³⁰ jeweils ein Wasserstoffatom, eine Arylgruppe mit 6 bis 20 Kohlenstoffatomen, eine Thienylgruppe oder eine Bithienylgruppe sind, R¹³ bis R¹⁸ bzw. R¹⁹ bis R²⁴ bzw. R²⁵ bis R³⁰ dasselbe oder verschieden sein können, D⁷ bis D¹² jeweils eine Arylgruppe mit 6 bis 20 Kohlenstoffatomen sind, welche mit einer elektronenabgebenden Gruppe, einer Thienylgruppe, einer Bithienylgruppe oder einer kondensierten polycyclischen Gruppe mit 10 bis 30 Kohlenstoffatomen substituiert ist, D⁷ bis D⁹, D¹⁰ und D¹¹ dasselbe oder verschieden sein können und Ar⁵ bis Ar¹⁰ und R¹³ bis R³⁰ jeweils unsubstituiert oder substituiert sein können mit einer Alkylgruppe mit 1 bis 10 Kohlenstoffatomen, einer Alkoxygruppe mit 1 bis 10 Kohlenstoffatomen, einer Aryloxygruppe mit 6 bis 10 Kohlenstoffatomen, einer Arylalkylgruppe mit 7 bis 10 Kohlenstoffatomen oder einer Aminogruppe mit einem Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen.

8. Funktionelle Schicht nach mindestens einem der Ansprüche 3 bis 7, wobei das Ladungsinjektions-Hilfsmaterial mindestens eines aus der elektronenabgebenden Gruppe und der kondensierten polycyclischen Gruppe aufweist, um so ebenfalls als Fluoreszenz-Dotiermittel zu fungieren.

45 9. Organische Elektronenvorrichtung, umfassend die funktionelle Schicht nach mindestens einem der Ansprüche 1 bis 8 und eine äußere Schicht.

10. Organische Elektronenvorrichtung nach Anspruch 9, welche eine organische Elektrolumineszenzvorrichtung ist.

50 11. Elektrolumineszenzvorrichtung nach Anspruch 10, wobei die funktionelle Schicht die lichtemittierende Schicht ist.

12. Elektrolumineszenzvorrichtung nach Anspruch 11, wobei die Ionisierungsenergie des Ladungsinjektions-Hilfsmaterials geringer ist als die Ionisierungsenergie der lichtemittierenden Schicht.

55 13. Elektrolumineszenzvorrichtung nach Anspruch 11 oder 12, wobei die Energiefülle des Ladungsinjektions-Hilfsmaterials geringer ist als die Energiefülle der lichtemittierenden Schicht.

14. Elektrolumineszenzvorrichtung nach mindestens einem der Ansprüche 11 bis 13, wobei das Ladungsinjektions-

Hilfsmaterial durch die Rekombination von positiven Löchern und Elektronen in der lichtemittierenden Schicht angeregt wird, wodurch das Material Licht emittiert.

5 15. Elektrolumineszenzvorrichtung nach mindestens einem der Ansprüche 11 bis 14, wobei die Energiefülle des Ladungsinjektions-Hilfsmaterials um mindestens 0,1 eV geringer ist als die Energiefülle der lichtemittierenden Schicht.

10 **Revendications**

1. Couche fonctionnelle d'un dispositif électronique organique, comprenant une substance hôte organique de transport de trou positif, qui est soumise à une injection de trou positif à partir d'une couche externe et possède des propriétés d'injection de trou positif améliorées par l'incorporation d'une matière auxiliaire d'injection de charge 15 composée d'un dérivé du stilbène, d'un dérivé du distyrylarylène ou d'un dérivé du tris(styrylarylène), ladite matière auxiliaire d'injection de charge étant présente en une quantité de 19% ou moins en poids, de préférence 0,05 à 9% en poids par rapport au poids de la substance hôte organique de transport de trou positif.

2. Couche fonctionnelle selon la revendication 1, dans laquelle la couche fonctionnelle est une couche luminescente, une couche d'injection de trou positif, une couche de transport de trou positif ou une couche barrière aux électrons. 20

3. Couche fonctionnelle selon la revendication 1 ou 2, dans laquelle le dérivé du stilbène, le dérivé du distyrylarylène ou le dérivé du tris(styrylarylène) possède au moins un groupe donneur d'électron.

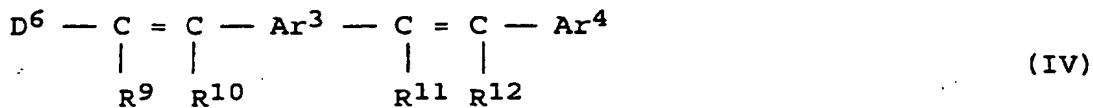
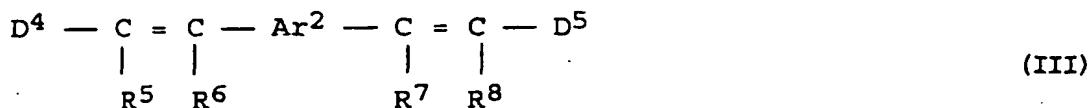
4. Couche fonctionnelle selon la revendication 3, dans laquelle le groupe donneur d'électron est choisi parmi un groupe alcoxy ayant 1 à 10 atomes de carbone, un groupe aryloxy ayant 6 à 20 atomes de carbone ou un groupe 25 amino avec un radical hydrocarboné ayant 1 à 30 atomes de carbone.

5. Couche fonctionnelle selon l'une quelconque des revendications 1 à 4, dans laquelle le dérivé de stilbène est un composé représenté par la formule générale (I) ou (II) : 30



45 dans laquelle Ar^1 est un groupe aryle ayant 6 à 20 atomes de carbone, un groupe thiényle ou un groupe bithiényle, R^1 à R^4 sont chacun un atome d'hydrogène, un groupe aryle ayant 6 à 20 atomes de carbone, un groupe thiényle ou un groupe bithiényle, R^1 et R^2 , et R^3 et R^4 peuvent respectivement, être chacun identiques ou différents, D^1 à D^3 sont chacun un groupe aryle ayant 6 à 20 atomes de carbone qui est substitué par un groupe donneur d'électron, un groupe thiényle, un groupe bithiényle ou un groupe polycyclique condensé ayant 10 à 30 atomes de carbone, D^2 et D^3 peuvent être identiques ou différents, et Ar^1 et R^1 à R^4 peuvent être chacun non substitués ou substitués 50 par un groupe alkyle ayant 1 à 10 atomes de carbone, un groupe alcoxy ayant 1 à 10 atomes de carbone, un groupe aryloxy ayant 6 à 10 atomes de carbone, un groupe arylalkyle ayant 7 à 10 atomes de carbone ou un groupe amino avec un radical hydrocarboné ayant 1 à 20 atomes de carbone.

55 6. Couche fonctionnelle selon l'une quelconque des revendications 1 à 4, dans laquelle le dérivé de distyrylarylène est un composé représenté par la formule générale (III) ou (IV) :



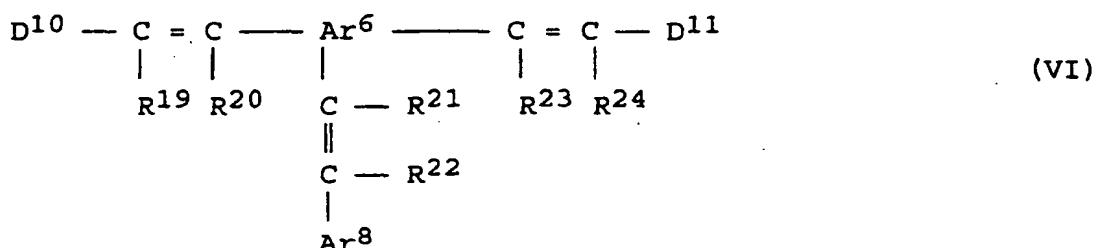
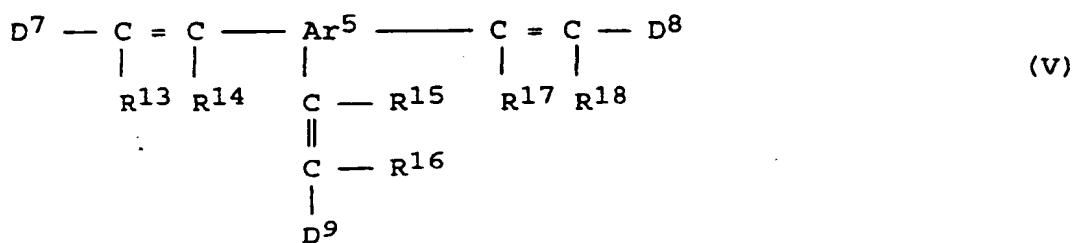
15 dans laquelle Ar^2 et Ar^3 sont chacun un groupe arylène ayant 6 à 20 atomes de carbone, un groupe thiénylène ou un groupe bithiénylène, Ar^4 est un groupe aryle ayant 6 à 20 atomes de carbone, un groupe thiényle ou un groupe bithiényle, R^5 à R^{12} sont chacun un atome d'hydrogène, un groupe aryle ayant 6 à 20 atomes de carbone, un groupe thiényle ou un groupe bithiényle, R^5 à R^8 , et R^9 à R^{12} peuvent respectivement être chacun identiques ou différents, , D^4 à D^6 sont chacun un groupe aryle ayant 6 à 20 atomes de carbone qui est substitué par un groupe donneur d'électron, un groupe thiényle, un groupe bithiényle ou un groupe polycyclique condensé ayant 10 à 30 atomes de carbone, D^4 et D^5 peuvent être identiques ou différents, et Ar^2 à Ar^4 et R^5 à R^{12} peuvent être chacun non substitués ou substitués par un groupe alkyle ayant 1 à 10 atomes de carbone, un groupe alcoxy ayant 1 à 10 atomes de carbone, un groupe aryloxy ayant 6 à 10 atomes de carbone, un groupe arylalkyle ayant 7 à 10 atomes de carbone ou un groupe amino avec un radical hydrocarboné ayant 1 à 20 atomes de carbone.

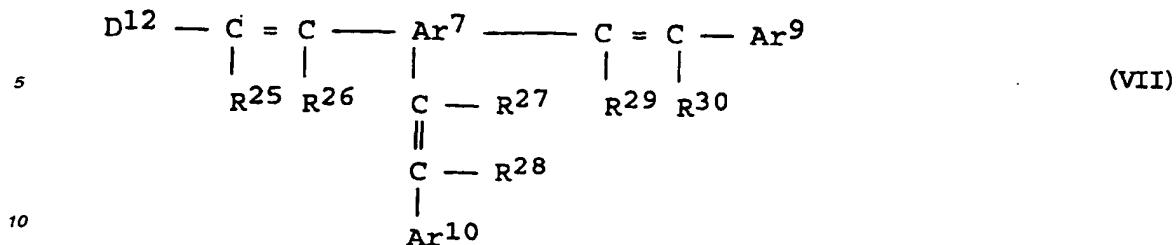
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7. Couche fonctionnelle selon l'une quelconque des revendications 1 à 4, dans laquelle le dérivé du tris(styrylarylène) est un composé représenté par la formule générale (V), (VI) ou (VII) :





15 dans lesquelles Ar⁵ à Ar⁷ sont chacun un radical cyclique trivalent ayant 6 à 24 atomes de carbone, Ar⁸ à Ar¹⁰ sont chacun un groupe aryle ayant 6 à 20 atomes de carbone, un groupe thiényle ou un groupe bithiényle, Ar⁹ et Ar¹⁰ peuvent être identiques ou différents, R¹³ à R³⁰ sont chacun un atome d'hydrogène, un groupe aryle ayant 6 à 20 atomes de carbone, un groupe thiényle ou un groupe bithiényle, R¹³ à R¹⁸ et R¹⁹ à R²⁴, et R²⁵ à R³⁰ peuvent respectivement être chacun identiques ou différents, , D⁷ à D¹² sont chacun un groupe aryle ayant 6 à 20 atomes de carbone qui est substitué par un groupe donneur d'électron, un groupe thiényle, un groupe bithiényle ou un groupe polycyclique condensé ayant 10 à 30 atomes de carbone, D⁷ à D⁹, D¹⁰ et D¹¹ peuvent être identiques ou différents, et Ar⁵ à Ar¹⁰ et R¹³ à R³⁰ peuvent être chacun non substitués ou substitués par un groupe alkyle ayant 1 à 10 atomes de carbone, un groupe alcoxy ayant 1 à 10 atomes de carbone, un groupe aryloxy ayant 6 à 10 atomes de carbone ; un groupe arylalkyle ayant 7 à 10 atomes de carbone ou un groupe amino avec un radical hydrocarboné ayant 1 à 20 atomes de carbone.

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25 8. Couche fonctionnelle selon l'une quelconque des revendications 3 à 7, dans laquelle la matière auxiliaire d'injection de charge possède au moins un élément parmi le groupe donneur d'électron et le groupe polycyclique condensé de façon à fonctionner également en tant que dopant fluorescent.

30 9. Dispositif électronique organique comprenant la couche fonctionnelle selon l'une quelconque des revendications 1 à 8 et une couche externe.

35 10. Dispositif électronique organique selon la revendication 9, étant un dispositif d'électroluminescence organique.

11. Dispositif d'électroluminescence selon la revendication 10, dans lequel la couche fonctionnelle est la couche luminescente.

40 12. Dispositif d'électroluminescence selon la revendication 11, dans lequel l'énergie d'ionisation de la matière auxiliaire d'injection de charge est inférieure à l'énergie d'ionisation de la couche luminescente.

13. Dispositif d'électroluminescence selon la revendication 11 ou 12, dans lequel la bande interdite de ladite matière auxiliaire d'injection de charge est plus petite que la bande interdite de la couche luminescente.

45 14. Dispositif d'électroluminescence selon l'une quelconque des revendications 11 à 13, dans lequel la matière auxiliaire d'injection de charge est excitée par la recombinaison de trous positifs et d'électrons dans la couche luminescente, de cette manière ladite matière émet de la lumière.

15. Dispositif d'électroluminescence selon l'une quelconque des revendications 11 à 14, dans lequel la bande interdite de la matière auxiliaire d'injection de charge est plus petite que la bande interdite de la couche luminescente d'au moins 0,1 eV.

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FIG. 1

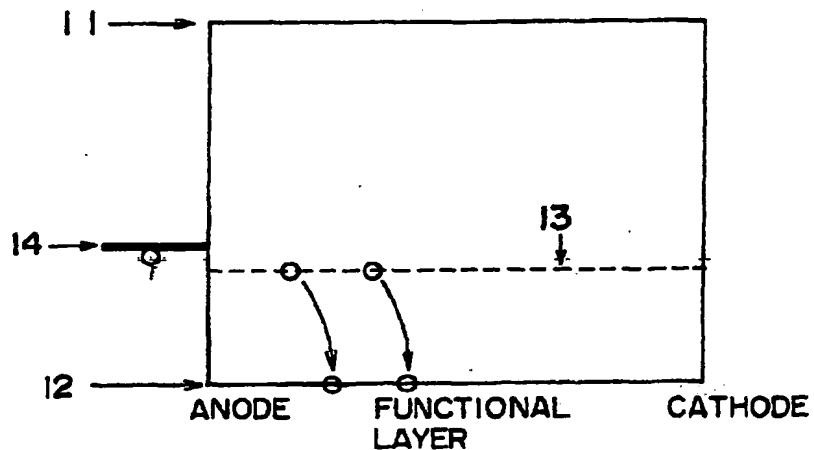
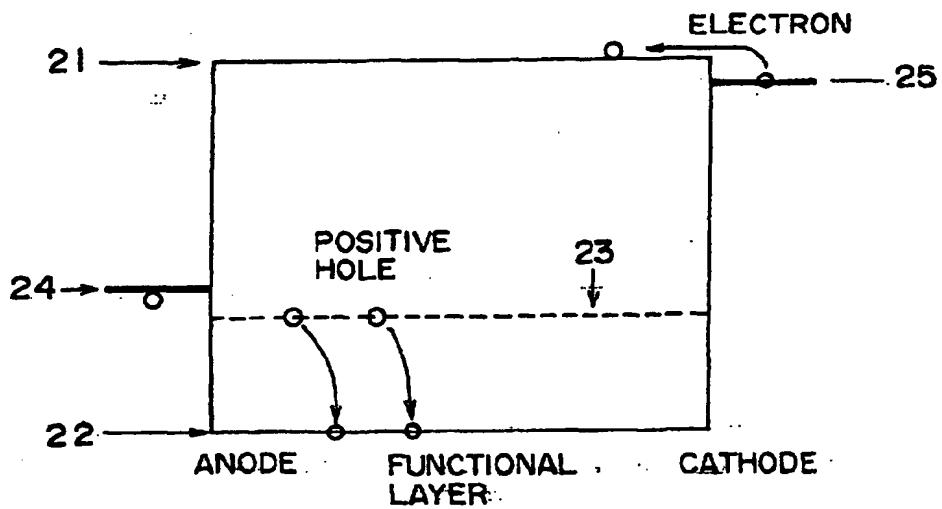


FIG. 2



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